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Steam

its generation and use

The Babcock & Wilcox Company
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Edited by J.B. Kitto and S.C. Stultz

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Chapter 21

Fuel Ash Effects on Boiler Design and Operation

The effective utilization of fossil fuels for power generation depends to a great extent on the capability of the steam generating equipment to accommodate the inert residuals of combustion, commonly known as *ash*. The quantity and characteristics of the ash inherent to a particular fuel are major concerns to both the designer and the operator of the equipment.

With few exceptions, most commercial fuels contain sufficient ash to warrant specific design and operating considerations. The following focuses on these design and operating considerations, primarily as they relate to pulverized coal firing. Fuel ash characteristics relating to petroleum fuels are also discussed.

Ash dilutes the heating value of fuel, placing additional burdens on fuel storage, handling and preparation equipment. Extensive facilities are also needed to collect, remove and dispose of the ash. These material handling requirements represent significant costs in terms of equipment and real estate which are directly proportional to the amount of ash in the fuel. In the case of coal, ash quantities can be substantial. Consider, for example, a 650 MW utility steam generator firing a coal with a heating value of 10,000 Btu/lb (23,250 kJ/kg) containing 10% ash by weight. The unit would burn approximately 300 tons per hour (272 t_m/h) of coal, generating more than 700 tons per day (635 t_m/d) of ash.

In pulverized coal-fired boilers, most of this ash is carried out of the furnace by the gaseous products of combustion (flue gas). Abrasive ash particles suspended in the gas stream can cause erosion problems on convection pass heating surfaces. However, the most significant ash-related problem is deposition. During the combustion process, the mineral matter that forms ash is released from the coal at temperatures in the range of 3000F (1649C), well above the melting temperature of most mineral matter compounds. Ash can be released in a molten fluid or sticky plastic state. A portion of the ash, which is not cooled quickly to a dry solid state, impacts on and adheres to the furnace walls and other heating surfaces. Because such large total quantities of ash are involved, even a small fraction of the total can seriously interfere with boiler operation. Accumulation of ash deposits on furnace walls impedes heat transfer, delaying cooling of the flue gas and increasing the flue gas temperature leaving the furnace. Elevated temperatures at the furnace exit raise steam temperature and can extend deposition problems to pendant superheaters and other heat absorbing surfaces in the convection pass. In extreme cases, uncontrolled ash deposits can develop to the point where flow passages in tube banks are blocked, impeding gas flow and ultimately requiring the unit to be shut down for manual removal. Large deposits in the upper furnace or radiant superheater can become dislodged and fall, damaging pressure parts in the lower furnace. Under certain conditions, ash deposits can also cause fireside corrosion on tube surfaces.

Minimizing the potential for these ash-related problems is a primary goal of both the designers and operators of coal-fired boilers. The extent to which coal ash characteristics affect boiler design is illustrated in Fig. 1 which compares the relative size of a gas-fired and coal-fired boiler. Both are sized for the same steam generating capacity and similar steam conditions. While the combustion characteristics of coal play a role in sizing the furnace, the deposition and erosion potential of the ash are the primary design considerations driving the overall size and arrangement.

The variability of ash behavior is one of the biggest problems for boiler designers and operators. Although boilers are often designed to burn a wide range of coals satisfactorily, no unit can perform equally well with all types of coal.

Ash content of coal

The ash content of coal varies over a wide range. This variation occurs not only in coals from different geographical areas or from different seams in the same region, but also from different parts of the same mine. These variations result primarily from the wide range of conditions that introduced foreign material during or following the formation of the coal. (See Chapter 9.) Ash content can also be influenced by extraneous mineral matter introduced during the mining operation. Before being sold, some commercial coals are cleaned or washed to remove a portion of what would be labeled ash in the laboratory. However, the ash content of significance to the user is the content at the point of use. The values noted below are on that basis.

Most of the coal used for power generation in the United States (U.S.) has an ash content between 6 and 20%. Low values of 3 to 4% in bituminous coals are rare and these coals find other commercial uses, particularly in the metallurgical field. On the other hand,

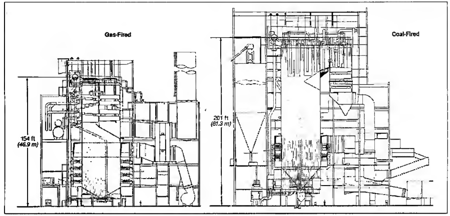


Fig. 1 Size comparison of gas-fired and coal-fired utility boilers.

some coals may have ash contents as high as 40%. Many high ash fuels can be successfully burned in utility (electric power generation) boilers. Their use has increased in areas where they offer an economic advantage.

Evaluation of ash content on a weight percentage basis alone does not take into account the heat input associated with the coal, which is also related to moisture content. It is common, for design and fuel evaluation purposes, to consider ash content on the basis of weight per unit of heat input, generally expressed as pounds of ash per million Btu. This factor is calculated as follows:

$$\frac{\text{Ash (\% by weight)}}{\text{HHV(Btu/lb)}} \times 10^4 = \text{lb ash}/10^6 \text{ Btu}$$

or (1)

$$\frac{\text{Ash (\% by weight)}}{\text{HHV (kJ/kg)}} \times 10^3 = \text{kg ash/MJ}$$

where HHV is the higher heating value of the fuel.

The relevance of this factor is illustrated in Table 1, which provides proximate analyses for three selected coals. Each coal has a moderate ash content of 9 to 10% by weight. However, on a heat input basis, ash quantities vary significantly. The lignite in this example would introduce almost three times as much ash as the high volatile bituminous coal at an equivalent heat input.

Furnace design for ash removal

Historically, two distinctly different types of furnace design were used to handle the ash from coal firing in large utility boilers. These are commonly referred to as the *dry-ash* or *dry-bottom* furnace and the *slag-tap* or *wet-bottom* furnace.

All modern pulverized coal-fired boilers use the dry-bottom arrangement. The coal-fired boiler in Fig. 1 is typical of this design. In a dry-bottom unit most of the ash, typically 70 to 80%, is entrained in the flue gas and carried out of the furnace. This portion of the ash is commonly known as *flyash*. Some of the flyash is collected in hoppers arranged under the economizer and air heaters, where coarse particles drop out of suspension when gas flow direction changes. The finer ash particles remain in suspension and are carried out of the unit for collection by particulate control equipment. (See Chapter 33.) The remaining 20 to 30% of the ash that settles in the furnace, or is dislodged from the furnace walls, is collected in a hopper formed by the frontwall and rearwall tube panels at the bottom of the furnace. This *bottom ash* is discharged through a 3 to 4 ft (0.9 to 1.2 m) wide opening that spans the entire width of the hopper.

Slag-tap furnaces were originally developed to resolve ash deposition and removal problems when firing coals with low ash fusion temperatures in dry-bottom furnaces. These units are intentionally de-

Table 1
Proximate Analyses of Three Selected Coals — Ash Content as Weight Per Unit of Heat Input

Rank	High Volatile Bituminous	Subbituminous	Lignite
Moisture, %	3.1	23.8	45.9
Volatile matter, %	42.2	36.9	22.7
Fixed carbon, %	45.4	29.5	21.8
Ash, %	9.4	9.8	9.6
Heating value, Btu/lb	12,770	8683	4469
lb Ash/10^6 Btu	7.4	11.3	21.5

signed to maintain ash in a fluid state in the lower furnace. Molten ash is collected on the furnace walls and other surfaces in the lower furnace and drained continuously to openings called *slag-taps* in the furnace floor. Water tanks positioned beneath the slag-taps solidify the liquid ash for disposal.

Slag-tap furnaces have been used with both pulverized coal and Cyclone™ furnace firing systems. (See Chapter 15.) Application is limited to coals having ash viscosity characteristics which would ensure that ash fluidity could be maintained over a reasonable boiler load range. Much of the coal ash research conducted by The Babcock & Wilcox Company (B&W) concerning the viscosity-temperature relationship of coal ash was initially directed at defining coal ash suitability limits for wet-bottom and Cyclone furnace applications. A minimum coal ash content was also specified to ensure sufficient ash quantities to maintain the required slag coating. One benefit of wet-bottom firing was a significant reduction in flyash quantity. In pulverized coal wet-bottom applications, as much as 50% of the total ash was collected in the furnace. Units equipped with Cyclone furnaces could retain up to 80% of the ash in the furnace.

The application of slag-tap units for pulverized coal firing began to decline in the late 1940s, primarily due to design improvements in dry-bottom units that minimized ash deposition problems. Slag-tap units equipped with Cyclone furnaces continued to be applied until the early 1970s when the federal Clean Air Act mandated control of nitrogen oxides (NO_x) emissions. The high furnace temperatures required for wet-bottom operation were highly conducive to NO_x formation.

Ash deposition

Regardless of the firing method, when coal is burned, a relatively small portion of the ash will cause deposition problems. Ash passing through the boiler is subject to various chemical reactions and physical forces which lead to deposition on heat absorbing surface. The process of deposition and the structure of deposits are variable due to a number of factors. Particle composition, particle size and shape, particle and surface temperatures, gas velocity, flow pattern and other factors influence the extent and nature of ash deposition.

Due primarily to the differences in deposition mechanisms involved, two general types of high temperature ash deposition have been defined as *slagging* and *fouling*.

Slagging is the formation of molten, partially fused or resolidified deposits on furnace walls and other surfaces exposed to radiant heat. Slagging can also extend into convective surface if gas temperatures are not sufficiently reduced.

Most ash particles melt or soften at combustion temperatures. The time-temperature history or cooling rate of the particle determines its physical state (solid, plastic or liquid) at a given location in the furnace. Generally, in order to adhere to a clean surface and form a deposit, the particle must have a viscosity low enough to wet the surface.

Slag deposits seldom form on clean tube surfaces. A conditioning period is required before significant deposition occurs. Assuming there is no direct flame impingement, as ash particles approach a clean tube, most tend to be resolidified due to the relatively lower temperature at the tube surface. The particles fracture on impact and partially disperse back into the flue gas stream. Over a period of time, however, a base deposit begins to form on the tube. The base deposit may be initiated by the settling of fine ash particles or the gradual accumulation of particles with very low melting point constituents. As the base deposit thickens, the temperature at its outside face increases significantly above the tube surface temperature. Eventually, the melting point of more of the ash constituents is exceeded and the deposit surface becomes molten. The process then becomes self-accelerating with the plastic slag trapping essentially all of the impinging ash particles. Ultimately, the deposit thickness reaches an equilibrium state as the slag begins to flow, or the deposit becomes so heavy that it falls away from the tubes. Depending on the strength and physical characteristics of the deposit, sootblowers using steam, compressed air or water as cleaning media (see Chapter 24) may be able to control or remove most of the deposit. However, the base deposit can remain attached to the tube, allowing subsequent deposits to accumulate much more rapidly.

Fouling is defined as the formation of high temperature bonded deposits on convection heat absorbing surfaces, such as superheaters and reheaters, that are not exposed to radiant heat. In general, fouling is caused by the vaporization of volatile inorganic elements in the coal during combustion. As heat is absorbed and temperatures are lowered in the convective section of the boiler, compounds formed by these elements condense on ash particles and heating surface, forming a glue which initiates deposition.

Areas where slagging and fouling can occur are shown in Fig. 2. Figs. 3 and 4 show heavily slagged and fouled surfaces. The characteristics of coal ash and their influence on slagging and fouling are discussed in the following sections.

Characteristics of coal ash

Sources of coal ash

Mineral matter is always present in coal and forms ash when the coal is burned. This mineral matter is usually classified as either inherent or extraneous. (See Chapter 9.) Inherent mineral matter is organically combined with the coal. This portion came from the chemical elements existing in the vegetation from which the coal was formed and from elements chemically bonded to the coal during its formation. Extraneous mineral matter is material that is foreign to the organic structure of the coal. This includes airborne and waterborne material that settled into the coal deposit during or after formation. It usually consists of mineral forms associated with clay, slate, shale, sandstone or limestone and includes pieces ranging from microscopic size to thick layers. Other extraneous material may be introduced through the mining process.

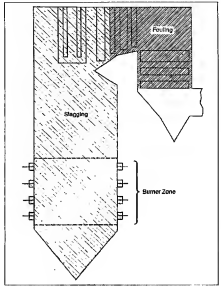


Fig. 2 Deposition zones in a coal-fired boiler.

Mineralogical composition

There are no standardized methods that are used routinely for determining the specific mineral constituents of coal. Mineralogical analysis requires the use of a low temperature ashing technique to separate the mineral matter from the organic portion of the coal. Standard high temperature ashing procedures would significantly alter the mineral forms. However, a number of researchers, using a variety of low temperature ashing methods and sophisticated analytical techniques, have identified an enormous variety of mineral species in coal, encompassing the entire spectrum of major mineral forms found in the earth's crust. Most of these minerals fall into one of several groups: clay minerals (aluminosilicates), sulfides/sulfates, carbonates, chlorides, silica/silicates and oxides. Some of the more common minerals in these groups are shown in Table 2.

Chemical composition

Because both quantitative and qualitative evaluation of mineral matter forms are extremely difficult, relatively simple chemical analyses are commonly used to determine the percentages of the major elements in the ash. Elemental ash analysis is performed on a coal ash sample produced in accordance with the American Society for Testing and Materials (ASTM) D 3174 ashing procedure. Pulverized coal is burned in a furnace with an oxidizing atmosphere at 1292 to 1382F (700 to 750C). The elements present in the ash are quantitatively measured using a combination of emission spectroscopy and flame photometry and are reported as weight percents of their oxides. Coal ash is consistently found to be composed mainly of silicon, aluminum, iron and calcium with smaller amounts of magnesium, titanium, sodium and potassium. The elemental analysis also identifies phosphorus as P_2O_5 and sulfur as sulfur trioxide (SO_3). Phosphorus is usually present in very small quantities and is sometimes omitted. Sulfur is reported as SO_3 because it is normally present as the sulfate form of one of the metals.

Percentages of the individual elements vary over a wide range for different coals; however, characteristic differences are evident between the older, high rank coals common in the Eastern U.S. and the younger, low rank Western coals. Bituminous coals typically have higher levels of silica, aluminum and iron, while the lower rank subbituminous coals and lignites generally have higher levels of the alkaline earth metals, calcium and magnesium, and the alkali metal sodium. These trends are evident in the ash analyses shown in Table 3.

Although the ash constituents are reported as oxides, they actually occur in the ash predominately as

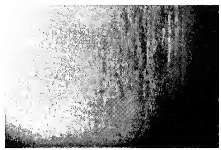


Fig. 3 Heavily slagged surface

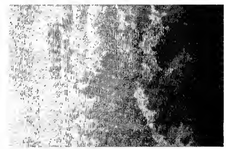


Fig. 4 Heavily fouled surface.

Table 2
Common Minerals Found in Coal

Clay minerals:	
Montmorillonite	$Al_2Si_4O_{10}(OH)_2 \cdot H_2O$
Illite	$KAl_2(AlSi_3O_{10})(OH)_2$
Kaolinite	$Al_4Si_4O_{10}(OH)_8$
Sulfide minerals:	
Pyrite	FeS_2
Marcasite	FeS_2
Sulfate minerals:	
Gypsum	$CaSO_4 \cdot 2H_2O$
Anhydrite	$CaSO_4$
Jarosite	$(Na,K)Fe_3(SO_4)_2(OH)_6$
Carbonate minerals:	
Calcite	$CaCO_3$
Dolomite	$(Ca,Mg)CO_3$
Siderite	$FeCO_3$
Ankerite	$(Ca,Fe,Mg)CO_3$
Chloride minerals:	
Halite	$NaCl$
Sylvite	KCl
Silicate minerals:	
Quartz	SiO_2
Albite	$NaAlSi_3O_8$
Orthoclase	$KAlSi_3O_8$
Oxide minerals:	
Hematite	Fe_2O_3
Magnetite	Fe_3O_4
Rutile	TiO_2

a mixture of silicates, oxides and sulfates, with smaller quantities of other compounds. The silicates originate mainly from quartz and the clay minerals which contribute silicon, aluminum, sodium and much of the potassium. A principal source of iron oxide is pyrite (FeS_2) which is oxidized to form Fe_2O_3 and sulfur oxides. Part of the organic and pyritic sulfur that is oxidized combines with calcium and magnesium to form sulfates. Calcium and magnesium oxides result from the loss of carbon dioxide from carbonate minerals such as calcite ($CaCO_3$) and dolomite [$(Ca, Mg)(CO_3)$]. In low rank coals, a major portion of the sodium, calcium and magnesium oxides can originate from organically bound elements in the coal.

Laboratory ash is prepared from a coal sample in a controlled atmosphere at controlled temperatures to provide a reproducible and uniform ash. The actual ashing process during combustion in a pulverized coal-fired furnace is a much more complex process. In a boiler furnace, pulverized coal is burned in suspension as discrete particles. If all of the mineral matter were evenly distributed through the coal, the composition of each resulting ash particle would be the same as the bulk ash composition determined by the analysis of ASTM ash. A coal with no extraneous mineral matter might approach this hypothetical case, because organically combined inherent material would be expected to be evenly distributed. In reality, however, all coals contain non-uniformly distributed extraneous mineral matter in some of the wide variety of mineral forms shown on Table 2. When the coal is pulverized, some of the particles will be mostly coal with only inherent mineral matter, some will be pure mineral matter, and others will be combinations of both. Because the coal particles are burned discretely in suspension, the composition of an individual ash particle will depend on the specific mineral form or forms that were included in the coal particle. As a result, individual particle composition can vary significantly from the bulk ash composition.

During combustion, ash particles are exposed to temperatures as high as 3000F (1649C) and a variety of heating and cooling rates. The atmosphere in the burner zone can range from highly oxidizing to highly reducing. Depending on the composition of the specific particle, mineral forms in the ash can react with each other, with the organic and inorganic constituents of the coal, and with gaseous elements, such as sulfur dioxide (SO_2), in the flue gas. The compounds that are ultimately formed by these interactions are the materials that cause deposition problems. The compounds can have a wide variety of melting temperatures and viscosity-temperature characteristics. Some compounds combine to form eutectic mixtures that have melting temperatures lower than either of the original compounds. Particles that melt at lower temperatures and stay sticky long enough to reach a furnace wall become slag deposits. Volatile compounds that vaporize in the furnace tend to condense on and foul cooler convective heating surfaces.

Elemental ash analyses do not directly identify the compounds that cause deposition, or directly identify the mechanisms of deposit formation. Despite these limitations, no other data pertaining to coal ash composition are as widely available as the chemical analyses of ASTM ash. A large part of the coal ash research that has been conducted over the last sixty years has been directed at correlating analysis data and other characteristics of ASTM ash to observed ash behavior both in full scale boilers and in test facilities that closely simulate full scale conditions. Various evaluation methods have been developed based on these correlations to characterize ash behavior and predict deposition potential.

Ash fusibility

The measurement of ash fusibility temperatures is by far the most widely used method for predicting ash behavior at elevated temperatures. The preferred procedure in the U.S. is outlined in ASTM Standard D 1857, *Fusibility of Coal and Coke Ash*. An ash sample is prepared by burning coal under oxidizing conditions at temperatures of 1470 to 1650F (799 to 899C). The ash is pressed in a mold to form a triangular pyramid (cone) 0.75 in. (19 mm) in height with a 0.25 in. (6.35 mm) triangular base. The cone is heated in a furnace at a controlled rate to provide a temperature increase of 15F (8C) per minute. The atmosphere in the furnace is regulated to provide either oxidizing or reducing conditions. As the sample is heated, the temperatures at which the cone fuses and deforms to specific

Table 3
Ash Content and Ash Fusion Temperatures of Some U.S. Coals and Lignite

Rank:	Low Volatile Bituminous	High Volatile Bituminous				Sub-bituminous	Lignite
Seam	Pocahontas No. 3	No. 9	No.6	Pittsburgh		Antelope	
Location	West Virginia	Ohio	Illinois	West Virginia	Utah	Wyoming	Texas
Ash, dry basis,%	12.3	14.1	17.4	10.9	17.1	6.6	12.8
Sulfur, dry basis, %	0.7	3.3	4.2	3.5	0.8	0.4	1.1
Analysis of ash, % by wt							
SiO_2	60.0	47.3	47.5	37.6	61.1	28.6	41.8
Al_2O_3	30.0	23.0	17.9	20.1	21.6	11.7	13.6
TiO_2	1.6	1.0	0.8	0.8	1.1	0.9	1.5
Fe_2O_3	4.0	22.8	20.1	29.3	4.6	6.9	6.6
CaO	0.6	1.3	5.8	4.3	4.6	27.4	17.6
MgO	0.6	0.9	1.0	1.3	1.0	4.5	2.5
Na_2O	0.5	0.3	0.4	0.8	1.0	2.7	0.6
K_2O	1.5	2.0	1.8	1.6	1.2	0.5	0.1
SO_3	1.1	1.2	4.6	4.0	2.9	14.2	14.6
P_2O_5	0.1	0.2	0.1	0.2	0.4	2.3	0.1
Ash fusibility							
Initial deformation temp, F							
Reducing	2900+	2030	2000	2030	2180	2280	1975
Oxidizing	2900+	2420	2300	2265	2240	2275	2070
Softening temp, F							
Reducing		2450	2160	2175	2215	2290	2130
Oxidizing		2605	2430	2385	2300	2285	2190
Hemispherical temp, F							
Reducing		2480	2180	2225	2245	2295	2150
Oxidizing		2620	2450	2450	2325	2290	2210
Fluid temp, F							
Reducing		2620	2320	2370	2330	2315	2240
Oxidizing		2670	2610	2540	2410	2300	2290

shapes, as shown in Fig. 5, are recorded. Four deformation temperatures are reported as follows:

1. *Initial deformation temperature* (IT or ID) – the temperature at which the tip of the pyramid begins to fuse or show signs of deformation.
2. *Softening temperature* (ST) – the temperature at which the sample has deformed to a spherical shape where the height of the cone is equal to the width at the base (H = W). The softening temperature is commonly referred to as the fusion temperature.
3. *Hemispherical temperature* (HT) – the temperature at which the cone has fused down to a hemispherical lump and the height equals one half the width of the base (H = 1/2 W).
4. *Fluid temperature* (FT) – the temperature at which the ash cone has melted to a nearly flat layer with a maximum height of 0.0625 in. (1.59 mm).

The determination of ash fusion temperatures is strictly an empirical procedure, developed in standardized form, which can be duplicated with some degree of accuracy. Strict observance of test conditions is required to assure reproducible results. ASTM specified tolerances on reproducibility of the individual temperature measurements range from 100 to 150F (56 to 83C) when the test is performed by different operators and apparatus.

An earlier version of the ASTM D 1857 procedure specified the use of only a reducing atmosphere and had loosely defined criteria for identifying the softening and fluid points. When the atmosphere is not specified, it is generally assumed to be reducing. Reported softening temperatures are assumed to be the ST (H = W) point unless otherwise specified. Methods for determining fusibility of ash used by other countries are similar to the ASTM procedure but results may vary considerably due to differences in procedures or the definition of terms.

The gradual deformation of the ash cone is generally considered to result from differences in melting characteristics of the various ash constituents. As the temperature of the sample is increased, compounds with the lowest melting temperatures begin to melt, causing the initial deformation. As the temperature continues to increase, more of the compounds melt and the degree of deformation proceeds to the softening and hemispherical stages. The process continues until the

Fig. 5 Specific shapes as ash fuses and deforms with temperature

temperature is higher than the melting point of most of the ash constituents and the fluid stage is reached.

Fusibility testing was originally developed to evaluate the clinkering (agglomerating) tendency of coal ash produced by combustion on a grate. In several respects, the test method is a somewhat better simulation of stoker firing than suspension burning of pulverized coal. During the fusion test, at a heating rate of 15F (8C) per minute, the transition from the IT to the FT stage may take up to two hours or more for a high fusion ash. Rather than slow heating and gradual melting of the ash, the process in a pulverized coal furnace is essentially reversed. Ash particles are rapidly heated, and then cooled at a relatively slow rate, as they pass through the furnace. During combustion, coal particles are heated almost instantaneously to temperatures ranging up to 3000F (1649C). As heat is removed from the flue gas, the ash is cooled over a period of less than two seconds to temperatures around 1900 to 2200F (1038 to 1204C) at the furnace exit.

In practical terms, for dry-bottom furnaces, fusion temperatures provide an indication of the temperature range over which portions of the ash will be in a molten fluid or semi-molten, plastic state. High fusion temperatures indicate that ash released in the furnace will cool quickly to a nonsticky state resulting in minimal potential for slagging. Conversely, low fusion temperatures indicate that ash will remain in a molten or plastic state longer, exposing more of the furnace surface or convective surface to potential deposition.

When temperatures in the furnace are below the measured initial deformation temperature, the majority of the ash particles are expected to be in a dry solid state. In this form, particles impacting on heating surface will bounce off and be re-entrained in the gas stream, or, at worst, settle on the surface as a dusty deposit which can be readily removed by sootblowers. At temperatures above the IT, the ash becomes increasingly more plastic in nature and impacting particles have a greater potential to stick to heating surfaces.

Fusibility temperatures also provide an indication of deposit characteristics as they relate to control and cleanability. When the temperature at a deposit surface is at or above the fluid temperature of the ash, slag will tend to flow or drip from the surface. While fluid slag can not be controlled with sootblowers, the deposits tend to be self-limiting in thickness and do not interfere significantly with heat transfer effectiveness. However, if the deposit surface temperature is in the plastic range, between the initial deformation and hemispherical temperatures, the slag will be too viscous to flow and will continue to build in thickness. Wide IT to HT differentials can result in deposits that build quickly to large proportions and are difficult to control, because sootblowers can be ineffective in penetrating the plastic shell that forms on the deposit surface.

In practice, very high and very low fusion values are relatively easy to interpret as being troublesome or non-troublesome with respect to slagging. Unfortunately, however, most coals fall in an intermediate range where evaluations can be much more difficult. Fusion temperatures have their most valid significance when used on a comparative basis against corresponding data from other fuels of known full-scale performance. Even comparisons can be misleading, however, when differences in data are within the range of reproducibility of the test. Actual ash viscosity measurements (described later) provide a much more accurate and less subjective definition of the viscosity/temperature relationship and are considered by B&W to provide a better assessment of slagging potential.

Influence of ash elements

Ash classification

Coal ash is classified into two categories based on its chemical composition. ***Lignitic*** ash is defined as having more (CaO + MgO) than Fe_2O_3. ***Bituminous*** ash is defined as having more Fe_2O_3 than the sum of CaO and MgO. Bituminous ash is generally characteristic of higher rank coals from the eastern U.S. Lower rank western coals typically have lignitic ash. As a result, bituminous ash is sometimes referred to as eastern ash and lignitic ash is sometimes referred to as western ash. However, ash classification is not specific to ASTM rank or geographical origin. In rare cases, lignites and subbituminous coals can have bituminous ash and bituminous coals can have lignitic ash. For example, the Utah coal shown in Table 3 is classified a bituminous, but has lignitic ash.

Effect of iron

Iron has a dominating influence on the slagging characteristics of coals with bituminous type ash. As shown in Table 2, iron can be present in coal in several mineral forms. These include pyrite (FeS_2), siderite ($FeCO_3$), hematite (Fe_2O_3), magnetite (Fe_3O_4) and ankerite [(Ca, Fe, Mg)CO_3]. Pyrite is the major form of iron in most Eastern coals. In areas of the furnace where there is sufficient oxygen, pyrite is converted to Fe_2O_3 and SO_2. If the local atmosphere is reducing, however, pyrrhotite (FeS) is formed along with the lesser-oxidized iron forms such as FeO and metallic iron, Fe. The reduced forms have significantly lower melting temperatures than the oxidized forms. When completely oxidized to Fe_2O_3 iron tends to raise all four values of ash fusion temperatures: initial deformation, softening, hemispherical and fluid. In the lesser oxidized form (FeO) it tends to lower all of these values. The effect of iron in each of these forms is indicated in Fig. 6, plotted for a large number of ash samples from U.S. coals. The data show that as the amount of iron in the ash increases, there is a greater difference in ash fusibility between oxidizing and reducing conditions.

These effects may be negligible with coal ash containing small amounts of iron. Coals with lignitic ash generally have small amounts of iron and the ash fusion temperatures are affected very little by the state of iron oxidation. In fact, lignitic ash containing high levels of calcium and magnesium may have ash fusion temperatures that are lower on an oxidizing basis than on a reducing basis. The ash analysis and fusion temperatures shown for the subbituminous coal in Table 3 illustrate this effect.

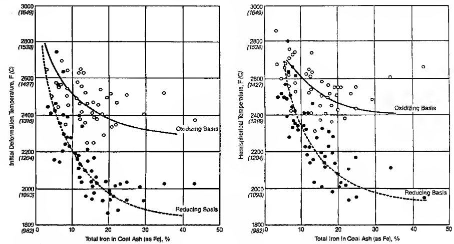


Fig. 6 Influence of iron on coal ash fusion temperatures.

Base to acid ratio

The constituents of coal ash can be classified as either basic or acidic. The basic constituents are iron, the alkaline earth metals calcium and magnesium, and the alkali metals sodium and potassium. Acidic constituents are silicon, aluminum and titanium. Bases and acids tend to combine to form compounds with lower melting temperatures. Experience has shown that the relative proportions of basic and acidic constituents provide an indication of the melting behavior and viscosity characteristics of coal ash.

The elemental analysis is used to calculate the percent base, percent acid and the base to acid ratio as follows:

$$\text{Percent base} = \frac{(Fe_2O_3 + CaO + MgO + Na_2O + K_2O) \times 100}{SiO_2 + Al_2O_3 + TiO_2 + Fe_2O_3 + CaO + MgO + Na_2O + K_2O} \quad (2)$$

$$\text{Percent acid} = \frac{(SiO_2 + Al_2O_3 + TiO_2) \times 100}{SiO_2 + Al_2O_3 + TiO_2 + Fe_2O_3 + CaO + MgO + Na_2O + K_2O} \quad (3)$$

$$\text{Base/acid ratio} = \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}{SiO_2 + Al_2O_3 + TiO_2} \quad (4)$$

The range of base to acid ratio extends from approximately 0.1 for highly acidic ash to 9.0 for ash that is high in base content.

Ash that is either highly acidic or highly basic generally has high ash fusion and melting temperatures. However, the presence of basic constituents in an acidic ash tends to flux or reduce the melting temperature and viscosity of the mixture. Conversely, the melting temperature and viscosity of a basic ash are reduced by relative proportions of acidic constituents. When the percent base and percent acid are nearly equal, fusion temperatures and ash viscosity tend to be reduced to minimum levels. The general trend is shown in Fig. 7. Minimum fusion temperatures typically occur at approximately 40 to 45% base which equates to base to acid ratios in the range of 0.7 to 0.8. Ratios in the range of 0.5 to 1.2 are generally considered to indicate high slagging potential.

The base to acid ratio considers all of the basic and acidic constituents to have equal effects on ash melting characteristics. However, research has shown that the various acids and bases have different fluxing strengths which must also be considered.

Studies conducted by B&W on the relationship of ash composition to ash viscosity have provided additional factors which improve the simple base to acid relationship. Ash viscosity is an important criterion for determining the suitability of a coal ash for use in a slag-tap furnace. Experience has shown that slag will flow readily at or below a viscosity of 250 poise. The temperature at which this viscosity occurs is called the T_{250} temperature of the ash. The preferred maximum T_{250} for wet-bottom applications is 2450F (1343C). Trends in T_{250} temperatures have been shown to correlate with ash fusion temperatures. Low T_{250} temperatures indicate low fusion temperatures and increased slagging potential.

Ash viscosity can be measured directly in a high temperature viscometer. Because viscosity measurements

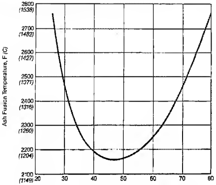


Fig. 7 Fusion temperatures and viscosities versus acidic constituents.

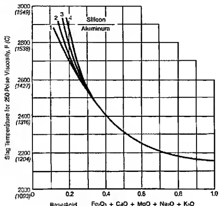


Fig. 8 Plot of temperature for 250 poise viscosity versus base to acid ratio – based on ferric percentage of 20.

require a considerable amount of coal ash that may not be readily available and are costly and time consuming, methods were developed to determine viscosity from chemical analysis of the coal ash. Based on a large number of direct viscosity measurements of bituminous and lignitic ash samples. T_{250} temperatures were related to ash composition as shown in Figs. 8 and 9. Fig. 8 is for bituminous ash and lignitic ash with an acidic content above 60%. At base to acid ratios less than 0.3, the silicon (SiO_2)/aluminum (Al_2O_3) ratio is taken into account. Silicon and aluminum are both acidic constituents; however, higher percentages of silicon tend to raise the T_{250} and the melting temperature.

Fig. 9 is for lignitic ash with an acidic content less than 60%. T_{250} is a function of both the percent base and the dolomite percentage which is defined as:

$$\text{Dolomite percentage} = \frac{(CaO + MgO) \times 100}{Fe_2O_3 + CaO + MgO + Na_2O + K_2O} \tag{5}$$

At a given percent base, higher dolomite percentages increase the T_{250} temperature, indicating that calcium and magnesium tend to raise ash viscosity and fusion temperature. Increasing amounts of the other base constituents (iron, sodium and potassium) tend to lower the T_{250} temperature.

Taken together, these trends indicate higher melting temperatures and higher viscosities at a given temperature for ash that is predominately composed of either silicon and aluminum or calcium and magnesium. Lower melting temperatures result from intermediate mixtures of these elements. However, in all combinations, iron, sodium and potassium act to flux the ash and increase the slagging potential.

As previously noted, the fluxing strength of iron is related to its state of oxidation. Metallic iron (Fe) and ferrous iron (FeO) are stronger fluxes than Fe_2O_3 and tend to reduce fusion temperatures and slag viscosity at a given temperature. The degree of iron oxidation is normally expressed as the ferric percentage where:

$$\text{Ferric percentage} = \frac{Fe_2O_3 \times 100}{Fe_2O_3 + 1.11FeO + 1.43Fe} \tag{6}$$

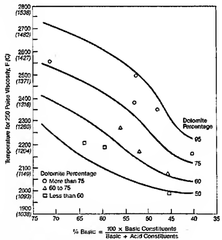


Fig. 9 Basic content and dolomite percentage of ash versus temperature for 250 poise viscosity.

The effect of ferric percentage on slag viscosity for a typical bituminous ash is shown in Fig. 10. Note that the T_{250} temperature can vary over a wide range depending on the degree of iron oxidation. Experience has shown that slag from boiler furnaces operating under normal conditions with 15 to 20% excess air has a ferric percentage of approximately 20%. The curves in Fig. 8 are based on this value.

Influence of alkalies on fouling

The alkali metals, sodium and potassium, have long been associated with the fouling tendencies of coal ash. Volatile forms of these elements are vaporized in the furnace at combustion temperatures. Subsequent reactions with sulfur in the flue gas and other elements in the ash form compounds that contribute to the formation of bonded deposits on convection heating surface.

Research conducted by B&W dating back to the 1950s identified a relationship between the total alkali content in bituminous coals and fouling potential. The specific laboratory procedure developed to establish this relationship, called the sintering strength test, is described in detail later in this chapter. Basically, the test involves measuring the compressive strength of flyash pellets heated in air for a period of time at temperatures of 1500 to 1800F (816 to 982C). The application of this method, combined with observations of fouling conditions in operating boilers, showed that high fouling coals produced flyash with high sintered strength. Conversely, low strength flyash was associated with low fouling coals. Correlation of standard ASTM ash analysis data with the sintering test results indicated a significant relationship (Fig. 11) between total alkali content (Na_2O and K_2O, expressed as equivalent total Na_2O) and flyash sintered strength. These correlations formed the basis for the first *fouling index* for bituminous coals which used the total alkali content in the coal to predict fouling potential.

Because ASTM ash produced in the laboratory could not be expected to represent the physical and chemical properties of flyash produced by full scale combustion, sintering strength testing required actual flyash samples aspirated from the flue gas in operating boilers. This meant full scale tests under steady-state conditions with a consistent coal supply, which became increasingly more difficult as unit size increased. To improve the efficiency and accuracy of obtaining data, a small laboratory ashing furnace (LAF) was constructed to burn pulverized coal at controlled conditions similar to those in a commercial boiler.

Subsequent tests on flyash produced in the LAF from a wide variety of bituminous coals demonstrated that sodium was the most important single factor affecting ash fouling. Potassium, which had been included in the previous alkali fouling indices, was found to make no significant contribution to sintering strength. Additionally, it was found that water soluble sodium, which was related to the more readily vaporized forms of sodium, had a major effect on sintered strength. This result was obtained by washing coals with hot condensate in the laboratory to remove the water soluble sodium. The washed coals were ashed in the LAF and sintered at various temperatures. Results for a high fouling Illinois coal are shown in Table 4. Water washing decreased the sodium content in the ash by approximately 70%, while the potassium content, which was initially higher than the sodium content, decreased by only 4%. Removing the soluble sodium resulted in a reduction in sintering strength at 1700F (927C) from 17,300 psi (119.3 MPa) for the raw coal to 550 psi (3.8 MPa) for the washed coal. Because the coal had a high chlorine content, it was concluded that most of the volatile sodium was probably in the form of NaCl. The insoluble potassium was likely associated with clay minerals or feldspar which would not readily decompose and vaporize during combustion.

The relationship of sintering strength to the percentage of soluble sodium in the ash was also found to be a function of the base to acid ratio, as shown in

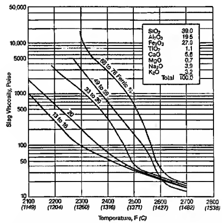


Fig. 10 Viscosity-temperature plots of a typical slag showing effect of ferric percentage.

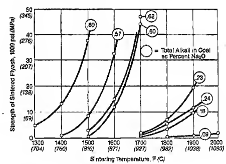


Fig. 11 Effect of alkali content in coal.

Table 4
Effect of Soluble Sodium on Sintered Strength

Ash Analysis	Raw Coal	Washed Coal
SiO_2	45.0	49.8
Al_2O_3	18.0	20.9
Fe_2O_3	21.0	22.9
TiO_2	0.8	1.0
CaO	8.8	1.6
MgO	0.9	1.0
Na_2O	1.6	0.5
K_2O	2.4	2.3
Ash sintered strength, psi (MPa)	17,300 (119.3)	550 (3.8)

Fig. 12. The combination of high sodium and high base to acid ratios resulted in the highest sintering strengths. Low ratios and sodium contents resulted in reduced flyash strength at the same sintering temperature. Similar trends were noted for variations in sintering strength as a function of base to acid ratio and total Na_2O in the ash. Statistical evaluations of these relationships were used to develop the fouling index currently used for coals with bituminous ash.

Similar tests on the sintering characteristics of lignitic ash indicated that the sintering criteria associated with fouling for bituminous ash did not apply to lignitic ash with high alkaline (CaO, MgO) contents. However, sintering strength was found to be directly proportional to the total sodium content in the ash shown in Fig. 13. Full scale and pilot scale tests conducted by the U.S. Bureau of Mines at the Grand Forks Coal Research Laboratory in North Dakota also established a correlation between fouling rate and sodium content for coals with lignitic ash. As shown in Fig. 14, deposition rates were found to increase sharply as the Na_2O content increased up to approximately 6% and then level off at higher percentages of sodium.

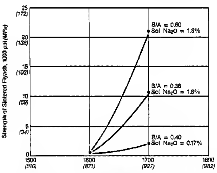


Fig. 12 Bituminous (Eastern) ash fouling effect of base to acid ratio and soluble sodium on sintered strength.

As previously noted, in low rank coals, a major portion of the alkali and alkaline earth metals can be organically bound in the coal. Because they are intimately mixed with the coal, it is believed that alkalies in this form are readily vaporized during combustion and play a dominating role in fouling. The organically associated elements occur in the form of cations chemically bonded to the organic structure of the coal. Ion exchange techniques have been developed to remove the cations from the coal for measurement. The method employed by B&W uses an ammonium acetate solution to provide a source of NH_4^+ ions which extract the ion-exchangeable cations. The laboratory procedure is described later in this chapter. Ion exchange data for a high fouling North Dakota lignite and a severe fouling Montana subbituminous coal are shown in Table 5. The data show that essentially all of the sodium in both coals is organically bound. In the lignite, the ion-exchangeable sodium actually exceeded the total sodium measured in ASTM ash. The difference most likely results from a loss of sodium due to vaporization during the high temperature ashing procedure. The relatively low percentages of ion-exchangeable K_2O indicate that most of the potassium exists in stable mineral forms.

Viscosity-temperature relationship of coal ash

The characteristics of slag deposits which form on furnace walls and other radiant surface are a function of deposit temperature and deposit composition.

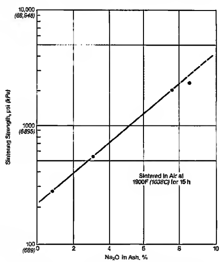


Fig. 13 Effect of Na_2O on sintering strength (North Dakota lignite ash).

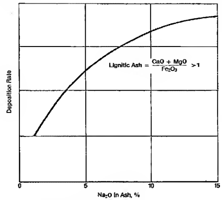


Fig. 14 Effect of Na_2O on deposition rate.

Deposit composition, in turn, is a function of the local atmosphere, particularly for ash with a significant iron content. Relationships between these factors determine the physical state of the deposit, which can range from a dry solid to plastic or even a viscous liquid if temperatures are sufficiently high. Dry deposits are usually not troublesome; they tend to be loosely bonded to the tube surface and relatively easy to remove by sootblowing. If deposits are allowed to build in thickness, the temperature increases and the surface of the deposit can become semi-molten or plastic. The plastic slag traps other transient ash particles and continues to build more and more rapidly as the surface temperature continues to increase. Ultimately, the deposit reaches an equilibrium state as the slag begins to flow.

Field experience has shown that plastic slag tends to form large deposits that are highly resistant to removal by conventional ash cleaning equipment. This

Table 5
Ion Exchange Data — High and Severe Fouling Coals

	Source:	North Dakota	Montana
	Rank:	Lignite	Subbituminous
Ash, dry basis, %		11.2	5.4
Total alkali, dry coal basis, %	Na_2O	4.25	6.74
	K_2O	0.37	0.65
Ion exchangeable alkali, dry coal basis, %	Na_2O	4.52	6.37
	K_2O	0.10	0.13
Relative ion exchange alkali, %	Na_2O	106%	95%
	K_2O	27%	20%

observation led to an extensive study of the relationship between ash viscosity and potential slagging tendency. Viscosity measurements that had previously been used to determine flow characteristics for wet-bottom furnace applications were extended to higher viscosity ranges to define the temperature range where a given ash would exhibit plastic characteristics.

As liquid ash is cooled, the logarithm of its viscosity increases linearly with decreasing temperature as shown in Fig. 15. At some point, the progression deviates from the linear relationship, and viscosity begins to increase more rapidly as the temperature continues to decrease. This transition into the plastic region is caused by the selective separation of solid material from the liquid, resulting from crystallization of the higher melting point constituents of the ash. The temperature at which this deviation takes place is called the temperature of critical viscosity (T_{cv}). T_{cv} varies depending on ash composition but normally occurs in a range between 100 and 500 poise. The end of the plastic region is the point of solidification, or freeze point, of the slag. The freeze point typically occurs at a viscosity of approximately 10,000 poise. For convenience in comparing the viscosity-temperature relationship of various ashes, the viscosity range of 250 to 10,000 poise has been defined as the plastic region.

The temperature at which the plastic region begins and the range of temperature over which the ash is plastic provide an indication of the slagging tendency. The lower the temperature within this range and the wider the range, the greater the potential for slagging. Viscosity-temperature curves for a high slagging Illinois coal and a low slagging east Kentucky coal, shown in Fig. 16, illustrate this effect. The plastic range for the Illinois coal begins at a relatively low temperature and extends over a wide temperature range. In contrast, the east Kentucky coal has a very narrow plastic range which begins at a much higher temperature. In comparison to the Illinois coal, the Kentucky coal ash would be expected to cool quickly below the temperature where the ash is plastic, exposing much less of the furnace to potential deposition.

As previously noted, the iron content of coal ash and its degree of oxidation have a significant influence on

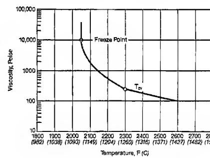


Fig. 15 Viscosity increase with decreasing temperature.

the viscosity of the ash. This effect is illustrated in Fig. 17 which shows the viscosity-temperature relationship for the high iron Illinois coal under both oxidizing and reducing conditions. Under reducing conditions, the viscosity at a given temperature is significantly lower and the ash remains plastic over a much wider temperature range.

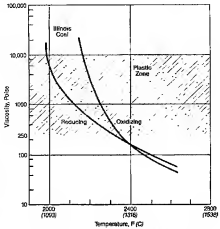


Fig. 17 Ash viscosity comparison – oxidizing and reducing conditions.

Ash reflectivity

Ash from certain coals produces furnace deposits that have reflective rather than insulating properties. This is particularly true of low sulfur, low sodium coals found in the western U.S., from the Powder River Basin in Wyoming and Montana. Reflective deposits can significantly reduce furnace heat absorption and increase furnace exit gas temperature even when only a very thin deposit is present. This can result in excessive radiant superheater slagging and fouling of convection surfaces. Experience has shown that reflective ash deposits can be difficult to remove and require special considerations in selection of ash cleaning equipment and media. (See Chapter 24.) Proprietary methods based upon field experience and laboratory studies are used to evaluate the potential for reflective ash formation, and to address the impact on furnace design and boiler performance.

Ash characterization methods

Several slagging and fouling indices have been developed by B&W to provide criteria for various aspects of boiler design. Slagging indices establish design criteria for the furnace and other radiant surface while fouling indices establish design criteria for convective surface. Deposition characteristics are generally classified into four categories: low, medium, high and severe.

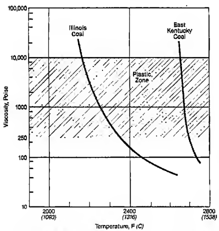


Fig. 16 Ash viscosity comparison for a high slagging and low slagging coal (oxidizing atmosphere).

For the most part, the indices described below are based on readily available ASTM ash analysis and fusibility data. In actual practice, when evaluating coals, designers take into account full scale experience on similar fuels and results of non-routine testing which can, in some cases, modify the classification. These indices can also be used on a comparative basis to rank coals with respect to their slagging and fouling potential when evaluating a new coal supply for an existing unit.

Ash classification

Because the characteristics of bituminous and lignitic ash vary significantly, the first step in calculating slagging and fouling indices is the determination of ash type. In accordance with the criteria previously described, ash is classified as bituminous when:

$$Fe_2O_3 > CaO + MgO \tag{7}$$

Ash is classified as lignitic when:

$$Fe_2O_3 < CaO + MgO \tag{8}$$

Slagging index – bituminous ash (R_s) Calculation of the slagging index (R_s) for bituminous ash takes into account the base to acid ratio and the weight percent, on a dry basis, of the sulfur in the coal. The base to acid ratio indicates the tendency of the ash to form compounds with low melting temperatures. The sulfur content provides an indication of the amount of iron that is present as pyrite. The calculation is as follows:

$$R_s = \frac{B}{A} \times S \tag{9}$$

where

B = $CaO + MgO + Fe_2O_3 + Na_2O + K_2O$
A = $SiO_2 + Al_2O_3 + TiO_2$
S = weight % sulfur, on a dry coal basis

Classification of slagging potential using R_s is as follows:

$R_s < 0.6$ = low
$0.6 < R_s < 2.0$ = medium
$2.0 < R_s < 2.6$ = high
$2.6 < R_s$ = severe

Slagging index – lignitic ash (R_s*) The slagging index for lignitic ash (R_s*) is based on ASTM ash fusibility temperatures. As previously noted, fusibility temperatures indicate the temperature range where plastic slag is likely to exist. The index is a weighted average of the maximum hemispherical temperature (HT) and the minimum initial deformation temperature (IT) as follows:

$$R_s^* = \frac{(\text{Max HT}) + 4\,(\text{Min IT})}{5} \tag{10}$$

where

Max HT = higher of the reducing or oxidizing hemispherical softening temperatures, F
Min IT = lower of the reducing or oxidizing initial deformation temperatures, F

Classification of slagging potential using R_s* is as follows:

$2450 < R_s^*$ = low
$2250 < R_s^* < 2450$ = medium
$2100 < R_s^* < 2250$ = high
$R_s^* < 2100$ = severe

Slagging index – viscosity (R_{vs}) As previously noted, B&W's most accurate method for predicting slagging potential is based on the viscosity-temperature relationship of the coal ash. This index (R_{vs}) is applicable to both bituminous and lignitic ash coals; however, measured ash viscosities are required.

$$R_{vs} = \frac{\left(T_{250\,oxid}\right) - \left(T_{10{,}000\,red}\right)}{97.5(fs)} \tag{11}$$

where

$T_{250\,oxid}$ = temperature, F, corresponding to a viscosity of 250 poise in an oxidizing atmosphere
$T_{10{,}000\,red}$ = temperature, F, corresponding to a viscosity of 10,000 poise in a reducing atmosphere

and fs is a correlation factor based on the average of the oxidizing and reducing temperatures (T_{fs}) corresponding to a viscosity of 2000 poise. Values for fs as a function of T_{fs} are provided in Fig. 18.

Classification of slagging potential using R_{vs} is as follows:

$R_{vs} < 0.5$ = low
$0.5 < R_{vs} < 1.0$ = medium
$1.0 < R_{vs} < 2.0$ = high
$2.0 < R_{vs}$ = severe

Fouling index – bituminous ash (R_f) The fouling index for bituminous ash is derived from sintering strength characteristics using the sodium content of the coal ash and the base to acid ratio as follows:

$$R_f = \frac{B}{A} \times Na_2O \tag{12}$$

where

B = $CaO + MgO + Fe_2O_3 + Na_2O + K_2O$
A = $SiO_2 + Al_2O_3 + TiO_2$
Na_2O = weight % from analysis of coal ash

Classification of fouling potential using R_f is as follows:

$R_f < 0.2$ = low
$0.2 < R_f < 0.5$ = medium
$0.5 < R_f < 1.0$ = high
$1.0 < R_f$ = severe

Fouling index – lignitic ash The fouling classification for lignitic ash coals is based on the sodium content in the ash as follows:

When $CaO + MgO + Fe_2O_3 > 20\%$ by weight of coal ash

$Na_2O < 3$ = low to medium
$3.0 < Na_2O < 6$ = high
$Na_2O > 6$ = severe

When $CaO + MgO + Fe_2O_3 < 20\%$ by weight of coal ash

$Na_2O < 1.2$ = low to medium
$1.2 < Na_2O < 3$ = high
$Na_2O > 3$ = severe

Coal ash effects on boiler design

Furnace design

The key to a successful overall gas-side design is proper sizing and arrangement of the furnace. As a first priority, the furnace must be designed to minimize slagging and to provide effective control of slag where and when it does form.

Ash deposition in the furnace can cause a number of problems. Slag deposits reduce furnace heat absorption and raise gas temperature levels at the furnace exit. This, in turn, can cause slagging and can aggravate fouling in the convection banks where ash deposits become increasingly more difficult to control as gas temperatures increase. The shift in heat absorption from the furnace to the superheater and reheater results in increased attemperator spray flow for control of steam temperatures, reducing cycle efficiency. Slag buildup at the top of a tall furnace is dangerous. Large deposits can become dislodged and fall, causing failures of furnace hopper tubes and loss of availability. Excessive slagging in the lower furnace can interfere with ash removal.

Experience has shown that several interrelated furnace design parameters are critical for slagging control. These parameters focus on keeping ash particles in suspension and away from furnace surfaces, distributing heat evenly to avoid high localized temperatures, and removing enough heat to achieve tempera-

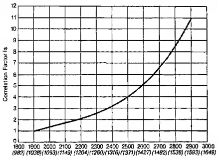


Fig. 18 Slagging index correction factor fs.

tures at the furnace exit that will minimize deposition on convection surface.

In the context of gas-side design, the furnace basically serves three functions. It must provide sufficient volume to completely burn the fuel, provide sufficient heat transfer surface to cool the flue gas and ash particles to a temperature suitable for admission to the convection surface, and minimize the formation of NO_x emissions (see Chapter 34). In general, for a coal-fired unit, it is the second criterion that determines the minimum furnace size.

The slagging classification of the coal establishes the upper limit on furnace exit gas temperature (FEGT) required to minimize the potential for slagging both in the radiant superheater and the close-spaced convection surface. As described in Chapter 22, furnace exit gas temperature is a function of furnace heat release rate. Limiting the FEGT, therefore, limits the heat release rate, resulting in lower average temperatures in the furnace. FEGT limits and corresponding heat release rates have been established by experience for different types of coal. In general, units using coals with low or medium slagging tendencies can have higher heat release rates and higher FEGTs. Units firing coals with high or severe slagging potential require lower heat release rates and lower FEGTs.

Ideally, the furnace would be an open box, sized with sufficient wall surface to cool the furnace gas and ash particles to the desired temperature before they reached any superheater surface. However, thermodynamic considerations in modern high pressure and high temperature cycles require that a significant portion of the total heat absorption be accomplished in the superheater and reheater. This requirement places a practical limit on the amount of furnace wall surface which, in a drum boiler, is dedicated to generating saturated steam. In order to achieve the required FEGT it becomes necessary to replace water-cooled furnace wall surface with steam-cooled superheater surface. These surfaces are generally in the form of widely spaced platens (see Chapter 19) located in the upper radiant zone of the furnace. Because platen surface is located in a relatively high gas temperature zone and subject to ash particle impaction, the side spacing must be sufficient to limit the potential for bridging and provide a degree of self-cleaning. Typical side spacing between platen sections is 4 to 5 ft (1.2 to 1.5 m). When platen superheater surface is used, the slagging classification of the coal establishes the upper limit on platen inlet gas temperature, in addition to limiting the FEGT.

An alternate method of controlling furnace exit gas temperature that has been widely used is gas tempering by flue gas recirculation. In this method, relatively cool gas from the economizer outlet is mixed with hot furnace gas near the furnace exit. Gas tempering offers a number of advantages. The FEGT can be limited with less furnace surface while the increased gas weight improves the thermal head for heat transfer, reducing the surface requirements in the convection pass. Proper introduction of the tempering flue gas provides a flat temperature profile at the furnace exit, reducing the possibility of localized slagging and fouling. Once the choice of gas recirculation is made, the system can also be used to control reheat steam temperature at partial loads. For this purpose, flue gas from the economizer outlet is introduced into the furnace through the furnace hopper opening. The cool gas reduces furnace heat absorption and makes more heat available to the reheater which offsets its natural characteristic of decreasing outlet steam temperature at partial loads.

The major disadvantages of gas recirculation are fan maintenance and power requirements. Fan erosion can be minimized to some extent by proper design and operation of a mechanical dust collector ahead of the fan. Extracting the recirculated gas after a hot precipitator offers the best potential for a relatively clean recirculated gas source.

In addition to having sufficient volume and heating surface, the furnace also must be correctly proportioned with respect to width, depth and height to minimize slagging. A significant design parameter in this regard is heat input from fuel to the furnace per unit of furnace plan area at the burners. Maximum limits on plan area heat release rate are a function of the slagging potential of the coal. Limits typically range from 1.5 to 1.8 × 10^6 Btu/h ft^2 (4.7 to 5.7 MW_t/m^2) for severe slagging and low slagging coals respectively.

The furnace must also be designed to limit the potential for ash particle impaction on furnace surfaces. Ample clearance must be provided between the burners and furnace walls as well as the furnace hopper and arch. These critical dimensions have been established by operating experience and keyed to the slagging classification of the coal.

The slagging classification also determines the locations, quantity and spacing of furnace wall blowers and long retractable sootblowers in the pendant radiant surface. (See Chapter 24.) These allow control of the deposition that inevitably occurs and are essential for maintaining furnace surface effectiveness and furnace exit gas temperature within the range provided for in the design. Some degree of slagging may be permitted above the burner zone but only to

the extent that it can be controlled by selective operation of the wall blowers. The control of these deposits can help maintain steam temperature at reduced loads. Slag deposits on furnace walls must be avoided below and between burners, however, where they can not be controlled by sootblowers.

Effect of slagging potential on furnace sizing

Referring to Fig. 19, three large utility boilers are shown sized for 660 MW at maximum continuous load. The boilers are assumed to have the same width for purposes of illustration, with the boiler setting height and furnace depth varied to accommodate the slagging characteristics of the different fuels. Boiler (a) is designed to fire a bituminous coal having a low to medium slagging potential. The slightly larger boiler (b) is designed to fire a subbituminous coal classified as having a high slagging potential. The difference in size can be attributed primarily to the difference in slagging potential. The furnace (b) depth has been increased to control slagging by reducing the input per plan area. The input and gas weight are higher for the subbituminous coal due to its higher moisture content and resulting lower boiler efficiency. This increases the required furnace surface and the furnace exit area to maintain acceptable gas velocities entering the convection pass. Comparing boiler (c), firing a severe slagging lignite, to boiler (b), the furnace depth has again been increased due to the increased slagging potential. The furnace surface has also been increased to reduce the gas temperature leaving the furnace. The size differential of the three units is quantified in Table 6. This table shows the proportionate differences or increases using boiler (a) as a base. Boiler (a) is assigned a size factor of 1.0 for the various parameters shown.

Convection pass design

The key to successfully preparing a design that will control convection pass fouling reverts back to a furnace design that will maintain the furnace exit gas temperature at predicted levels. Temperature excursions at the furnace exit result in corresponding higher temperature levels throughout the convection pass which can cause deposition problems even with coals which normally would be considered to have a low or moderate fouling tendency.

In general, convective heating surface, both pendant and horizontal, is arranged to minimize the potential for bridging and obstruction of the gas lanes between adjacent sections. The minimum clear side spacing (measured perpendicular to the gas flow) between sections in a bank varies as a function of the average flue gas temperature entering the bank. The widest spacing is required in the superheater banks which are in close proximity to the furnace exit, where the gas temperature and fouling potential are high. As the flue gas temperature is reduced, the side spacing in succeeding banks can also be reduced. The specific side space dimensions at a given temperature entering the bank depend on the fouling classification of the coal. Severe fouling coals require the widest spacing. Adequate side spacing must be maintained even in low temperature horizontal banks such as economizers. While these surfaces are not normally subject to bonded deposits, sufficient clear space must be maintained between sections to ensure that accumulations of ash dislodged from upstream surfaces will not bridge and plug the gas lanes. (See Chapter 20.)

Bank depths (measured parallel to the direction of gas flow) are established as a function of fouling potential, clear side spacing and the temperature enter-

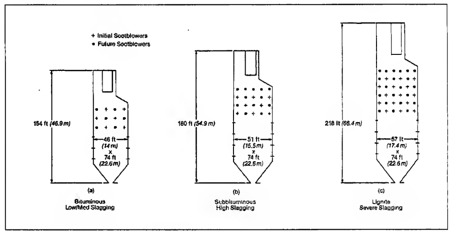


Fig. 19 Influence of slagging potential on furnace size. (See Table 6.)

Table 6
Boiler Size Versus Slagging Classification

	Boiler		
	(a)	(b)	(c)
Coal Rank	Bituminous	Subbituminous	Lignite
Slagging	Low/Med	High	Severe
Furnace plan area	1.0	1.11	1.24
Furnace surface	1.0	1.18	1.50
No. of furnce wall blowers	30	36	70

ing the bank. Cavities between the banks provide locations for long retractable sootblowers. At high gas temperatures, shallow bank depths are required to ensure adequate sootblower effectiveness. Sootblower jet penetration increases as temperatures are reduced and bank depths can be increased incrementally in cooler areas.

Flyash erosion

The metal loss on convection pass tubes due to flyash erosion is proportional to the total ash quantity passing through the boiler and is an exponential function of flue gas velocity. While with a given fuel there is no control of the ash quantity, erosion problems can be eased by reducing flue gas velocities. Velocity limits are determined based on the ash quantity on a pounds per million Btu (kg/MW$_t$) basis and the relative proportion of abrasive constituents in the ash. Typical limits range from 65 ft/s (19.8 m/s) for relatively non-abrasive low ash coals to 45 ft/s (13.7 m/s) or less for coals with high ash quantities and/or abrasive ash.

Effect of operating variables

Although the predominant factors affecting deposition are ash characteristics and boiler design, operating variables can also have a significant impact on slagging and fouling.

In general, operating variables associated with combustion optimization (see Chapter 14) tend to reduce the potential for deposition problems. These variables include air distribution, fuel distribution, coal fineness and excess air.

Air and fuel imbalances can result in high excess air at some burners while others operate with less than theoretical air. This, in turn, results in localized reducing conditions in the burner zone which can aggravate slagging, especially with coals having high iron content. High coal/air ratios can also delay combustion and upset heat distribution, resulting in elevated temperatures in the upper furnace and at the furnace exit. Long burnout times also increase the potential for burning particles to contact furnace walls and other heat transfer surfaces.

Secondary air imbalances can be minimized by adjusting individual burner flows to provide a flat O_2 profile at the economizer outlet. Care must be exercised to avoid burner adjustments that cause flame impingement on furnace walls. On the fuel side, burner line resistances should be balanced to maintain uniform coal flow to each burner. Coal feeders should be calibrated and adjusted to provide uniform coal flow to each pulverizer.

Low pulverizer fineness (see Chapter 13) can also cause problems associated with delayed combustion. Coarse particles require longer residence times for burnout and can cause slagging in the lower furnace.

Excess air has a tempering effect on average temperatures within the furnace and on furnace exit temperature. Excess air also reduces the potential for localized reducing conditions in the furnace when it is introduced through the burners. Air infiltration into the furnace or convection pass is far less beneficial and should be corrected or taken into account when establishing excess air requirements. While there is an associated efficiency loss, raising excess air above normal design levels is usually an effective tool for controlling deposition problems. In some cases, high excess air may also upset superheater/reheater absorption and steam temperatures.

Sootblowers (see Chapter 24) are the primary means of dealing directly with furnace wall slagging and convection pass fouling. The most important fundamental requirement is to use this equipment in a preventive, rather than corrective, manner. Sootblowers are most effective in controlling dry, loosely bonded deposits which typically occur in the early stages of deposition. If furnace slag is allowed to accumulate to the point that it becomes plastic or wet, or if convection pass deposits are allowed to build and sinter for long periods of time, removal becomes much more difficult. Sootblower sequencing requirements must be established by initial operating experience and updated when required, especially when fuel characteristics change. Boiler diagnostic systems, which are discussed in the following section, can assist in optimizing sootblower operation.

The least desirable operating technique for controlling deposition problems is load reduction. The most severe situations may require a permanent derate. However, in many marginal situations, temporary load reductions during off peak periods may provide sufficient cooling to shed slag and allow sootblowers to regain effectiveness.

Application of advanced diagnostic and control systems

Awareness of slagging and fouling conditions is critical to achieving reliability and availability on a coal-fired utility boiler. However, boiler surface cleanliness has been, traditionally, one of the most difficult operating variables to quantify. Typical indications of surface fouling appear to the operator indirectly in the form of steam temperatures, spray attemperation flows and draft losses (gas resistance). In some cases, experienced operators who are familiar with the operating characteristics of a unit can make judgments on slagging and fouling conditions based on operating conditions, but these secondary indications can be misleading. For example, the furnace can be slagged, causing undesirably high gas temperatures entering the convection surface. However, the steam temperatures and spray attemperation may be normal if the convection surfaces are also fouled.

Another indication of surface cleanliness is draft loss. By watching draft loss across a bank, an alert operator can determine that sootblowing is probably required. Usually, however, by the time a change in draft loss is detected across widely spaced pendant sections, the banks are already bridged and it may be too late for removal by the sootblowers.

Visual observation is frequently used to further quantify cleanliness conditions. In many instances, however, access is limited and subjective evaluations can leave considerable room for error. Advanced methods have been developed to overcome these shortcomings and to improve upon traditional time-based sootblowing control.

Computer based performance monitoring systems can provide a direct and quantitative assessment of furnace and convective surface cleanliness. B&W's Heat Transfer Manager™ (HTM) program is based on the heat transfer analysis program developed over many years for boiler design and validated by extensive empirical data. The HTM program is configured on a boiler-specific basis, taking into account the arrangement of the furnace and all convective surface. Measurements of temperatures, pressures, flows, and gas analysis data are used to perform heat transfer analysis in the furnace and convective section on a bank by bank basis.

Advanced intelligent sootblowing systems have also been developed to combine this real time assessment of furnace and convective surface cleanliness with closed loop control of the cleaning equipment. B&W's Powerclean™ system automatically determines where and when sootblowing should occur in the furnace and convection pass. Powerclean uses cleanliness data from the HTM program in an expert decision making structure that dictates when blowers should be cycled.

Intelligent systems such as Powerclean recognize problem areas early in their development, so that selective sootblowing can be directed at a specific problem area and ash cleaning equipment is operated based on need. Intelligent sootblowing systems can optimize blowing medium use and improve performance while reducing tube damage and providing consistency to boiler operations.

Slagging can be particularly troublesome in localized areas of the furnace. To help optimize wall cleaning, heat flux sensors can be used. These sensors are installed in the waterwalls of the furnace and provide a differential temperature across the wall which changes in proportion to the amount of deposition. Sensor data is integrated into the overall intelligent sootblowing system so that cleanliness can be optimized in the furnace region. If an array of sensors is installed, the furnace can be broken into regions for better control of wall cleaning equipment and to optimize operation.

Additional discussion of the application of control systems to local sootblower cleaning requirements is provided in Chapter 24.

Non-routine ash evaluation methods

The following describes the laboratory equipment and test procedures, referenced earlier, that are used to supplement the standard ASTM coal ash characterization methods.

Laboratory ashing furnace

As noted, the ASTM ashing procedure does not duplicate the ashing process that actually occurs in a boiler. A laboratory ashing furnace (LAF) provides a means to obtain flyash and deposit samples that are comparable to those obtained from full scale installations operating under similar conditions.

B&W's LAF, shown in Fig. 20, is designed to fire pulverized coal at rates typically between 5 and 10 lb/h (2.3 and 4.5 kg/h). The facility consists of a fuel feed system, pulverized coal burner and a refractory lined chamber. The combustion chamber is surrounded by an electrically heated guard furnace which controls the rate of heat removal from the chamber to simulate full scale furnace temperatures. The firing rate is established to approximate full scale furnace residence time. A deposition section located at the furnace exit contains air- or water-cooled probes. The surface temperature of the probes can be adjusted to simulate furnace and superheater tube operating temperatures.

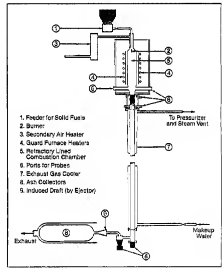


Fig. 20 Schematic of laboratory ashing furnace (LAF).

The probes are instrumented to allow measurement of metal temperatures, cooling fluid flow rates, and cooling fluid inlet and outlet temperatures. These data permit calculation of the total heat flux from the flue gas through the deposit and into the probe. The deposition section is also fitted with sootblowers to evaluate the effectiveness of ash removal equipment. Fig. 21 shows ash particles impacting a simulated superheater tube during a deposition test. The B&W LAF was used to develop extensive data which has now been correlated to the ash characteristics. These correlations have largely replaced the need for routine laboratory testing.

Measurement of ash viscosity

Viscosity of coal ash is measured in a high temperature rotating-bob viscometer (Fig. 22). The ash under study is contained in a cylindrical platinum-rhodium crucible, and a cylindrical bob is rotated in the liquid at a constant speed through a calibrated suspension wire. The torque or amount of twist produced in the suspension wire is proportional to the viscosity. The amount of twist is measured and recorded as the interval between impulses from light beams reflected from mirrors attached to the ends of the wire. The suspension wires are calibrated against viscosity standard oils obtained from the Bureau of Standards.

The electrically heated furnace is of the Globar tube type with temperature regulation provided through a controlling type potentiometer actuated by a thermocouple located in the furnace adjacent to the sample crucible. A thermocouple imbedded in the ash crucible support indicates sample temperature. Provision is made for controlling the atmosphere within the furnace. Ash is introduced into the crucible at an elevated temperature [2600 to 2800F (1427 to 1538C)] and held at that temperature until it becomes uniformly fluid. The temperature is then decreased in predetermined steps and the viscosity of the ash is measured at each temperature.

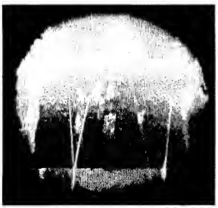


Fig. 21 Deposit formation on simulated superheater tube

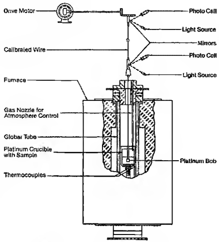


Fig. 22 Section through furnace of high temperature viscometer.

Ash sintering strength

The sintering strength test is performed on a flyash sample prepared in the LAF under a standard set of firing conditions. The flyash is passed through a 60 mesh (U.S. standard) (250 micron) screen to remove any particles of slag and then ignited to constant weight at 900F (482C) to remove any carbon that might be present. The ignited ash is then reduced to a minus 100 mesh size and at least 24 cylindrical specimens [0.6 in. (15.2 mm) diameter by 0.85 in. (21.6 mm) long] are formed in a hand press at a pressure of 150 psi (1034 kPa). At least six specimens are heated in air, usually at each of four temperature levels [1500, 1600, 1700 and 1800F (816, 871, 927 and 982C)] for 15 hours.

After the specimens have cooled slowly in the furnace, they are removed, measured and then crushed in a standard metallurgical testing machine. The sintered or compression strength is then computed from the applied force and the cross-sectional area of the sintered specimen. The average strength of six specimens is used as the strength of the sintered flyash at a particular sintering temperature.

Measurement of ion exchangeable cations in coal

Twenty grams of an air-dried minus 60 mesh coal sample are mixed with 100 ml of 1 N ammonium acetate in a 300 ml three-neck round bottom flask. A thermometer is inserted into the slurry. The slurry is stirred constantly and heated to 60 ±5C. The coal slurry sample is refluxed for 18 hours. The sample is filtered through a cellulosic filter media with 0.45 µ average pore size and washed twice with 25 ml of 1 N ammonium acetate solution.

The above procedure is repeated on the filtered coal except that the time is shortened to three hours. The combined filtrates are acidified by adding 2% by volume of glacial acetic acid and stored for inductive coupled plasma atomic emission spectrometric (ICPAES) analysis of Na, K, Ca and Mg.

Coal ash corrosion

Serious external wastage or corrosion of high temperature superheater and reheater tubes was first encountered in coal-fired boilers in 1955. Tube failures resulting from excessive thinning of the tube walls, as shown in Fig. 23, occurred almost simultaneously in the reheater of a dry ash furnace boiler and the secondary superheater of a slag-tap furnace unit. Corrosion was confined to the outlet tube sections of the reheater and the secondary superheater, which were made from chromium ferritic and stainless steel alloys, respectively.

Significantly, these boilers were among the first to be designed for 1050F (566C) main and reheat steam temperatures; also, both units burned high sulfur, high alkali Central and Southern Illinois coals, which were causing chronic ash fouling problems at the time.

Early investigations showed that corrosion occurred where complex alkali sulfates concentrated on tube surfaces beneath bulky layers of ash and slag. When dry, the complex sulfates were relatively innocuous; but when semi-molten [1100 to 1350F (593 to 732C)], they corroded the alloy steels used in superheater construction, and also other normally corrosion resistant alloys.

At first, it appeared that coal ash corrosion might be confined to boilers burning high alkali coals, but complex sulfate corrosion was soon found on superheaters and reheaters of several boilers burning low to medium alkali coals. Where there was no corrosion, the complex sulfates were either absent or the tube metal temperatures were moderate [less than 1100F (593C)]. The general conclusions drawn from this survey of corrosion were:

1. All bituminous coals contain enough sulfur and alkali metals to produce corrosive ash deposits on superheaters and reheaters, and those containing more than 3.5% sulfur and 0.25% chlorine may be particularly troublesome.
2. Experience has shown that corrosion rate is affected by both tube metal temperature and gas temperature. Fig. 24, which is used as a guide in design, indicates stable and corrosive zones of fuel ash corrosion as a function of gas and metal temperatures.

Based on this information, B&W modified the design of its boilers to greatly reduce the corrosion of superheaters and reheaters. These modifications included changes in furnace geometry, burner configuration, superheater arrangement and the use of gas tempering, all of which reduced metal and gas temperatures and reduced temperature imbalances. Experience from these installations has shown that it is possible to operate boilers with main and reheat steam temperatures up to 1050F (566C) with little, if any, corrosion from most coals.

Meanwhile, there was a gradual return to the 1000F (538C) steam conditions, due primarily to economic factors and secondarily to coal ash corrosion. This temperature level has permitted the use of lower cost alloys in the boiler, steam piping and turbine, with substantial savings in investment costs; it also has provided a greater margin of safety to avoid corrosion. Steam temperatures remained on the 1000F (538C) plateau for several decades. However, improved alloy creep and corrosion resistance and the potential for

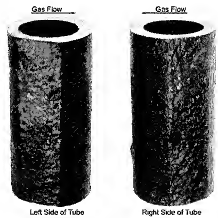


Fig. 23 Typical corroded 18Cr-8Ni tube from secondary superheater

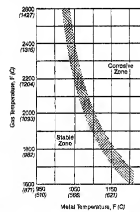


Fig. 24 Coal ash corrosion – stable and corrosive zones

cycle efficiency improvement have led to increased steam temperatures in the newest generation of utility boilers. Some recent boilers have been designed with main and reheat steam temperatures at and above 1100F (593C), and temperatures of 1200F (640C) and above are envisioned.

General characteristics of corrosion

External corrosion of superheaters and reheaters is concentrated on the upstream side of the tube, as shown in Fig. 25. The greatest metal loss usually occurs on the 10 and 2 o'clock sectors of the tubes, and it tapers off to little or none on the back side of the tubes. The corroded surface of the tube is highly sculptured by a shallow macropitting type of attack. The amount of corrosion, as measured by reduction in tube wall thickness, varies considerably along the length of the tube, depending on local conditions, i.e., the position of the tube in the bank or platen, the proximity of sootblowers, the composition of ash deposits and, most importantly, the gas and metal temperatures.

The corrosion rate is a nonlinear function of metal temperature (Fig. 26). Typically, the corrosion of both chromium ferritic and 18Cr-8Ni stainless steels increases sharply above a temperature of 1150F (621C), passes through a broad maximum between 1250 and 1350F (677 and 732C) and then decreases rapidly at still higher temperatures. However, the corrosion behavior varies depending on gas and ash chemistries and other factors, as well as temperatures.

The highest corrosion rates are generally found on the outlet tubes of radiant superheater or reheater platens opposite retractable sootblowers. Values ranging from 50 to 250 mils/yr (1.27 to 6.35 mm/yr) have been observed on 18Cr-8Ni stainless steel tubes under these adverse conditions. When similar high temperature surfaces [1100 to 1175F (593 to 635C)] are arranged in convection tube banks so they are shielded from direct furnace radiation and sootblower action, corrosion rates are much lower, ranging between 5 and 20 mils/yr (0.13 to 0.51 mm/yr).

Corrosive ash deposits

Corrosion is rarely found on superheater or reheater tubes having only dusty deposits. It is nearly always associated with sintered or slag type deposits that are strongly bonded to the tubes. Such deposits consist of at least three distinct layers. The outer layer, shown diagrammatically in Fig. 27, constitutes the bulk of the deposit and has an elemental composition similar

Fig. 25 Transverse sections of corroded tubes from secondary superheater platens.

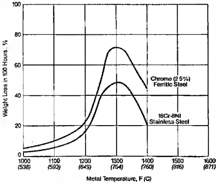
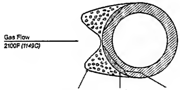


Fig. 26 Effect of temperature on corrosion rate.

to that of flyash. Though often hard and brittle, this layer is a porous structure through which gases may diffuse. Innocuous by itself, it plays an important part in the formation of an intermediate layer that contains the corrosive agents.

The intermediate layer, frequently called the white layer, is a white to yellow colored material which varies in thickness from 0.03 to 0.25 in. (0.76 to 6.35 mm). It usually has a chalky texture where corrosion is mild or nonexistent, but is fused and semi-glossy where corrosion is severe. In the latter condition this layer is difficult to remove as it is so firmly bonded to the corroded surface beneath.



	Outer Layer % by wt	Intermediate Layer % by wt	Inner Layer % by wt
SiO_2	23.5	23.3	7.6
Al_2O_3	14.0	11.5	1.7
Fe_2O_3	36.0	11.0	70.5
TiO_2	0.9	<0.1	<0.1
CaO	1.3	<0.1	<0.1
MgO	1.3	1.1	<0.1
Na_2O	0.3	1.7	0.15
K_2O	2.9	13.5	1.3
NiO	<0.1	<0.1	0.3
Cr_2O_3	<0.1	<0.1	7.0
SO_3	7.3	27.5	10.0
Cl	0.02	<0.01	<0.01
Water Soluble, %	9.0	45.4	9.0
pH	3.0	2.2	4.3
Excess SO_3, %	0.5	11.2	11.8

Fig. 27 Analyses of typical ash deposit from 18Cr-8Ni superheater tube.

Upon heating in the air, the intermediate layer melts around 1000F (538C) and slowly discolors and hardens into a hard mass resembling rust. Chemical analyses of this layer show that it contains higher concentrations of potassium, sodium and sulfur than does the parent coal ash. A large part of this deposit is water soluble and the water soluble fraction is always acidic. The most common compounds found are $Na_3Fe(SO_4)_3$ and $KAl(SO_4)_2$.

Complex alkali sulfates, when molten, rapidly corrode most, if not all, superheater alloys. Corrosion begins between 1000 and 1150F (538 and 621C), depending on the relative amounts of complex sodium and potassium sulfates present and whether these are predominantly iron or aluminum base compounds. Corrosion usually begins at the lower temperature where the sodium-iron-sulfate system is the major part of the intermediate layer, but corrosion is more severe and persists into a higher temperature range when the potassium-aluminum-sulfate system dominates.

If the intermediate layer is carefully removed, a black, glassy inner layer is revealed, which appears to have replaced the normally protective oxide on the tube. This layer is composed primarily of corrosion products, i.e., oxides, sulfides, and sulfates of iron and other alloying constituents in the tube metal. It seldom exceeds 0.063 in. (1.59 mm) thickness on corroded 18Cr-8Ni stainless steel tubes, probably because of its strong tendency to spall when the tubes cool. The layer containing corrosion products from chromium ferritic steels often reaches 0.125 in. (3.18 mm) thickness and exhibits little tendency to spall as the tube cools.

Corrosion mechanisms

The elements in coal ash corrosion (sodium, potassium, aluminum, sulfur and iron) are derived from the mineral matter in coal. The minerals supplying these elements include shales, clays and pyrites which are commonly found in all coals.

During the combustion of coal, these minerals are exposed to high temperatures and strongly reducing effects of carbon for very short periods of time. Although comparatively stable, the mineral matter undergoes rapid decomposition under these conditions. Some of the alkalies are released or volatilized as relatively simple compounds, which have dew points in the 1000 to 1300F (538 to 704C) range. Furthermore, sulfur in the coal is oxidized, releasing SO_2 with the formation of a small amount of SO_3, leaving a residue of iron oxide (Fe_2O_3).

By far the largest portion of the mineral matter or its derived species react to form the glassy particulates of flyash. The flyash and volatile species in the flue gases deposit on the tube surfaces. Slowly, over a period of weeks, the alkalis and the sulfur oxides diffuse through the layer of flyash toward the tube surface. In the lower temperature zone of the ash deposit, chemical reactions between the alkalis, the sulfur oxides, and the iron and aluminum components of the flyash form complex alkali sulfates as follows:

$$3K_2SO_4 + Fe_2O_3 + 3SO_3 \rightarrow 2K_3Fe(SO_4)_3$$

and

$$K_2SO_4 + Al_2O_3 + 3SO_3 \rightarrow 2KAl(SO_4)_2 \quad (13)$$

Similar reactions occur with sodium sulfate (Na_2SO_4), although the complex sodium sulfates are less apt to form at high temperatures because of their lower stability.

Work at B&W has shown that SO_3 concentrations in ash deposits must be very high (1000 to 1500 ppm) compared to the level in the flue gas (10 to 25 ppm) in order to form the complex alkali sulfates in the intermediate layer. Therefore, the bulk of the SO_3 must come from the catalytic oxidation of SO_2 in the outer layer of the deposit.

When the SO_3 produced in the outer deposit exceeds the partial pressure of SO_3 necessary for stability, the complex sulfates form through the above reactions. When the opposite is true, the complex sulfates begin to decompose according to the reverse of these reactions until a new equilibrium is reached. Because the formation of SO_3 is temperature dependent, the reversibility of these reactions is also temperature dependent. As shown in Fig. 26 the corrosion rate increases with temperature, passes through a maximum between 1250 and 1350F (677 and 732C), and then falls to a comparatively low level at higher temperatures.

The temperature range of this rapid liquid-phase attack is bracketed by: 1) the melting temperature of the mixture of complex alkali sulfates present, and 2) their thermal stability limits. The extreme width of this temperature band is approximately 400F (222C); corrosion due to the complex alkali sulfates may range from as low as 1000F (538C) to a maximum of 1400F (760C), depending on the species present in the intermediate layer.

Corrective measures

Various methods of combating corrosion of superheater and reheater tubes have been used or suggested, including the following:

1. the use of stainless steel shields to protect the most vulnerable tubes,
2. coal selection,
3. improvement of combustion conditions, i.e., providing proper coal fineness, fast ignition, good mixing and proper excess air, and
4. the use of more corrosion resistant alloys and alloy cladding on the most vulnerable superheater and reheater tubes. (See Chapter 19.)

New high chromium content stainless steels are generally more resistant to coal ash corrosion, but added chromium tends to degrade other metallurgical properties. New modified 25% chromium 20% nickel stainless steels offer improved performance for moderate conditions. Higher chromium nickel-based alloys and cladding offer maximum resistance for the most severe conditions.

Fuel oil ash

The ash content of residual fuel oil seldom exceeds 0.2%, an exceedingly small amount compared to that in coal. Nevertheless, even this small quantity of ash

is capable of causing severe problems of deposition and corrosion in boilers. Of the many elements that may appear in oil ash deposits, the most important are vanadium, sodium and sulfur. Compounds of these elements are found in almost every deposit in boilers fired by residual fuel oil and often constitute the major portion of these deposits.

Origin of ash

As with coal, some of the ash-forming constituents in the crude oil had their origin in animal and vegetable matter from which the oil was derived. The remainder is extraneous material, resulting from contact of the crude oil with rock structures and salt brines, or is picked up during refining processes, storage and transportation. (See Chapter 9.)

In general, the ash content increases with increasing asphaltic constituents in which the sulfur acts largely as a bridge between aromatic rings. Elemental sulfur and hydrogen sulfide have been identified in crude oil, and simpler sulfur compounds are found in the distillates of crude oil including thioesters, disulfides, thiophenes and mercaptans.

Vanadium, iron, sodium, nickel and calcium in the fuel oil were probably derived from the rock strata but some elements, such as vanadium, nickel, zinc and copper, probably came from organic matter from which the petroleum was derived. Vanadium and nickel especially are known to be present in organo-metallic compounds known as porphyrins which are characteristic of certain forms of animal life. Table 7 indicates the amounts of vanadium, nickel and sodium present in residual fuel oils from various crudes.

Crude oil as such is not normally used as a fuel but is further processed to yield a wide range of more valuable products. For example, in a modern U.S. refinery, 92.4% of the crude is converted to lighter fraction fuels and products such as gasoline, leaving 7.6% of residual fuel oil or distillate residue. Virtually all metallic compounds and a large part of the sulfur compounds are concentrated in the distillation residue. Where low sulfur residual fuel oils are required, they are obtained by blending with suitable stocks, including both heavy distillates and distillation from low sulfur crudes. This procedure is also used occasionally if a residual fuel oil must meet specifications such as vanadium or ash content.

Table 7
Vanadium, Nickel and Sodium Content of Residual Fuel Oils (ppm by wt)

Source of Crude Oil	Vanadium	Nickel	Sodium
Africa:			
1	5.5	5	22
2	1	5	–
Middle East:			
3	7	–	1
4	173	51	–
5	47	10	8
U.S.:			
6	13	–	350
7	6	2.5	120
8	11	–	84
Venezuela:			
9	–	6	480
10	57	13	72
11	380	60	70
12	113	21	49
13	93	–	38

Release of ash during combustion

Residual fuel oil is preheated and atomized to provide enough reactive surface so that it will burn completely within the boiler furnace. (See Chapter 11.) The atomized fuel oil burns in two stages. In the first stage the volatile portion burns and leaves a porous coke residue and in the second stage the coke residue burns. In general, the rate of combustion of the coke residue is inversely proportional to the square of its diameter, which in turn is related to the droplet diameter. Therefore, small fuel droplets give rise to coke residues that burn very rapidly, and the ash forming constituents are exposed to the highest temperatures in the flame envelope. The ash forming constituents in the larger coke residues from the larger fuel droplets are heated more slowly, partly in association with carbon. Release of the ash from these residues is determined by the rate of oxidation of the carbon.

During combustion, the organic vanadium compounds in the residual fuel oil thermally decompose and oxidize in the gas stream to V_2O_3, V_2O_4 and finally V_2O_5. Although complete oxidation may not occur and there may be some dissociation, a large part of the vanadium originally present in the oil exists as vapor phase V_2O_5 in the flue gas. The sodium, usually present as chloride in the oil, vaporizes and reacts with sulfur oxides either in the gas stream or after deposition on tube surfaces.

Subsequently, reactions take place between the vanadium and sodium compounds, with the formation of complex vanadates having melting points lower than those of the parent compounds; for example:

$$Na_2SO_4 + V_2O_5 \rightarrow 2NaVO_3 + SO_3\uparrow \qquad (14)$$

Melting points: 1625F 1275F 1165F

Excess sodium or vanadium in the ash deposit, above that necessary for the formation of the sodium vanadates (or vanadylvanadates), may be present as Na_2SO_4 and V_2O_5, respectively.

The sulfur in residual fuel oil is progressively released during combustion and is promptly oxidized to SO_2. A small amount of SO_2 is further oxidized to SO_3 by a small amount of atomic oxygen present in the hottest part of the flame. Also, catalytic oxidation of SO_2 to SO_3 may occur as the flue gases pass over vanadium rich ash deposits on high temperature superheater tubes and refractories. (See Chapter 35.)

Oil slag formation and deposits

The deposition of oil ash constituents on the furnace walls and superheater surfaces can be a serious problem. This deposition, coupled with corrosion of super-

heater and reheater tubes by deposits, was largely responsible for the break in the trend towards higher steam temperatures that occurred in the early 1960s.

Practically all boiler installations are typically designed for steam temperatures in the 1000 to 1015F (538 to 546C) range to minimize those problems and to avoid the higher capital costs of the more expensive alloys required in the tubes, steam piping and turbine for 1050 to 1100F (566 to 593C) steam conditions.

There are many factors affecting oil ash deposition on boiler heat absorbing surfaces. These factors may be grouped into the following interrelated categories: characteristics of the fuel oil, design of the boiler, and operation of the boiler.

Characteristics of fuel oil ash

Sodium, sulfur and vanadium are the most significant elements in the fuel oil because they can form complex compounds having low melting temperatures, 480 to 1250F (249 to 677C), as shown in Table 8. Such temperatures fall within the range of tube metal temperatures generally encountered in furnace and superheater tube banks of many oil-fired boilers. However, because of its complex chemical composition, fuel oil ash seldom has a single sharp melting point, but rather softens and melts over a wide temperature range.

An ash particle that is in a sticky, semi-molten state at the tube surface temperature may adhere to the tube if it is brought into contact by the gas flow over the tube. Even a dry ash particle may adhere due to mutual attraction or surface roughness. Such an initial deposit layer will be at a higher temperature than that of the tube surface because of its relatively low thermal conductivity. This increased temperature promotes the formation of adherent deposits. Therefore, fouling will continue until the deposit surface temperature reaches a level at which all of the ash in the gas stream is in a molten state, so that the surface is merely washed by the liquid without freezing and continued buildup.

In experimental furnaces, it has been found that the initial rate of ash buildup was greatest when the sodium-vanadium ratio in the fuel oil was 1:6, but an equilibrium thickness of deposit [0.125 to 0.25 in. (3.175 to 6.35 mm)] was reached in approximately 100 hours of operation. When the fuel oil contained more refractory constituents, such as silica, alumina and iron oxide, in addition to sodium and vanadium, an equilibrium condition was not reached and the tube banks ultimately plugged with ash deposits. However, these ash deposits were less dense, i.e., more friable, than the glassy slags encountered with a 1:6 sodium-vanadium fuel oil. Both the rate of ash buildup and the ultimate thickness of the deposits are also influenced by physical factors such as the velocity and temperature of the flue gases and particularly the tube metal temperature.

In predicting the behavior of a residual oil insofar as slagging and tube bank fouling are concerned, several fuel variables are considered including: 1) ash content, 2) ash analysis, particularly the sodium and vanadium levels and the concentration of major constituents, 3) melting and freezing temperatures of the ash, and 4) the total sulfur content of the oil. Applying this information in boiler design is largely a matter of experience.

Boiler design

Generally speaking, progressive fouling of furnaces and superheaters should not occur as long as the ash characteristics are not severe compared to the tube metal temperatures. If such trouble is encountered, the solution can usually be found in improving combustion conditions in the furnace and/or modifying the sootblowing procedures.

Studies on both laboratory and field installations have shown that the rate of ash deposition is a function of the velocity and temperature of the flue gases and the concentration of oil ash constituents in the flue gases. The geometry of the furnace and the spacing of tubes in the convection banks are selected in the design of a boiler to minimize the rate of deposition. It is common practice to use in-line tube arrangements with wider lateral spacings for tubes located in higher gas temperature zones. This makes bridging of ash deposits between tubes less likely and facilitates cleaning of tube banks by the sootblowers.

Boiler operation

Poor atomization of the fuel oil results in longer flames and frequently increases the rate of slag buildup on furnace walls which, in turn, makes it more difficult to keep the convection sections of the boiler clean. Completing combustion before the gases pass over the first row of tubes is especially important.

Table 8
Melting Points of Some Oil Ash Constituents

Compound	Melting Point, F	(C)
Aluminum oxide, Al_2O_3	3720	(2049)
Aluminum sulfate, $Al_2(SO_4)_3$	1420*	(771)
Calcium oxide, CaO	4662	(2572)
Calcium sulfate, $CaSO_4$	2640	(1449)
Ferric oxide, Fe_2O_3	2850	(1566)
Ferric sulfate, $Fe_2(SO_4)_3$	895*	(479)
Nickel oxide, NiO	3795	(2091)
Nickel sulfate, $NiSO_4$	1545*	(841)
Silicon dioxide, SiO_2	3130	(1721)
Sodium sulfate, Na_2SO_4	1625	(885)
Sodium bisulfate, $NaHSO_4$	480*	(249)
Sodium pyrosulfate, $Na_2S_2O_7$	750*	(399)
Sodium ferric sulfate, $Na_3Fe(SO_4)_3$	1000	(538)
Vanadium trioxide, V_2O_3	3580	(1971)
Vanadium tetroxide, V_2O_4	3580	(1971)
Vanadium pentoxide, V_2O_5	1275	(691)
Sodium metavanadate,		
$Na_2O \cdot V_2O_5(NaVO_3)$	1165	(629)
Sodium pyrovanadate, $2Na_2O \cdot V_2O_5$	1185	(641)
Sodium orthovanadate, $3Na_2O \cdot V_2O_5$	1560	(849)
Sodium vanadylvanadates,		
$Na_2O \cdot V_2O_4 \cdot V_2O_5$	1160	(627)
$5Na_2O \cdot V_2O_4 \cdot 11V_2O_5$	995	(535)

* Decomposes at a temperature around the melting point.

Relatively large carbonaceous particles have a far greater tendency to impinge on the tubes than do the smaller ash particles. If these larger particles are in a sticky state, they will adhere to the tubes where oxidation will proceed at a slow rate with consequent formation of ash. Fouling from this cause is difficult to detect by inspection during boiler outages because the carbonaceous material has usually disappeared completely. It can generally be detected during operation because flames are usually long and smoky, and *sparklers* may be carried along in the flue gases.

Regular and thorough sootblowing can have a decisive effect on superheater and reheater fouling. (See Chapter 24.) To be fully effective, however, sootblowing cycles should be frequent enough so that ash deposits can not build to a thickness where their surfaces become semi-molten and difficult to remove. In instances of extreme slagging, it is sometimes necessary to relocate sootblowers, to install additional sootblowers to control deposition in a critical zone, or to use additives.

The boiler load cycle can also have a significant effect on the severity of slagging and superheater fouling. A unit that is base loaded for long periods is more apt to have fouling problems on a borderline fuel oil than a unit that takes daily swings in load. In the latter instance, the furnace generally remains cleaner due to periodic shedding of slag, with the result that the gas temperatures through the superheaters are appreciably lower. This eases the burden on the sootblowers and substantially controls ash deposit formation in the superheater-reheater tube banks. Overloading the boiler, even for an hour or two a day, should be avoided, especially if excess air has to be lowered to the point where some of the burners are starved of air. The furnace is apt to become slagged and ash deposition can creep into the superheater and reheater tube banks.

Oil ash corrosion

High temperature corrosion

The sodium-vanadium complexes, usually found in oil ash deposits, are corrosive when molten. A measurable corrosion rate can be observed over a wide range of metal and gas temperatures, depending on the amount and composition of the oil ash deposit. Fig. 28 shows the combined gas and metal temperature effects on corrosion for a specific fuel oil composition of 150 ppm vanadium, 70 ppm sodium and 2.5% sulfur. As the vanadium concentration of the fuel oil varies, the amount of corrosion, compared to a 150 ppm vanadium fuel, will increase or decrease according to the curve shown in Fig. 29. The effect of the sodium level in the fuel oil is not as clear. The sodium content does, however, definitely affect the minimum metal temperature at which corrosion will be significant.

At the present time there appears to be no alloy that is immune to oil ash corrosion. In general, the higher the chromium content of the alloy, the more resistant it is to attack. This is the main reason for the use of 18Cr-8Ni alloys for high temperature superheater tubes. High chromium contents, greater than 30%, give added corrosion resistance but at the expense of physical properties; 25Cr-20Ni has been used as a tube cladding but even this alloy has not provided complete protection. High-nickel high-chromium alloys may be more resistant to oil ash attack under oxidizing conditions, but the higher material cost must be justified by longer life, which is not always predictable.

Low temperature corrosion

In oil-fired boilers, the problem of low temperature corrosion resulting from the formation and condensation of sulfuric acid from the flue gases is similar to that previously described for coal firing.

Oil-fired boilers are more susceptible to low temperature corrosion than are most coal-fired units for two reasons: 1) the vanadium in the oil ash deposits is a good catalyst for the conversion of SO_2 to SO_3, and 2) there is a smaller quantity of ash in the flue gases. Ash particles in the flue gas react with and reduce the amount of SO_3 vapor in the gas, and oil has considerably less ash than coal. Furthermore, coal ash is more basic than oil ash and more effectively neutralizes acid.

Methods of control

The methods of control that have been used or proposed to control fouling and corrosion in oil-fired boilers are summarized in Table 9, but in every instance economics govern their applicability. There is no doubt that reducing the amount of ash and sulfur entering the furnace is the surest means of control and that minimizing the effects of the ash constituents, once they have deposited on the tubes, is the least reliable. Because the severity of fouling and corrosion depends not only on the fuel oil characteristics but also on boiler design and operating variables, a generalized solution to these problems can not be prescribed.

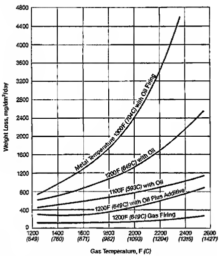


Fig. 28 Effect of gas and metal temperatures on corrosion of 304, 316 and 321 alloys in a unit fired with oil containing 150 ppm vanadium, 70 ppm sodium and 2.5% sulfur. Test duration 100 hours

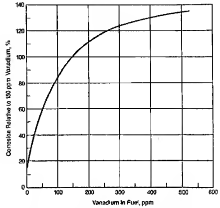


Fig. 29 Effect of vanadium concentration on oil ash corrosion.

Fuel oil supply

Although fuel selection and blending are practiced to some extent in the U.S., the common purpose is to provide safe and reliable handling and storage at the power plant rather than to avoid fouling difficulties. Because the threshold limits of sodium, sulfur and vanadium are not well defined for either fouling or corrosion, use of these means of control can not be fully exploited.

Fuel oil additives

An approach that is effective where the fuel oil ash is most troublesome involves adding, to the fuel or furnace, small amounts of materials that change the character of the ash sufficiently to permit its removal by steam or air sootblowers or air lances.

Additives are effective in reducing the problems associated with superheater fouling, high temperature ash corrosion and low temperature sulfuric acid corrosion. Most effective are alumina, dolomite and magnesia. Kaolin is also a source of alumina. Analyses of typical superheater deposits from a troublesome fuel oil, before and after treating it with alumina or dolomite, are shown in three bar graphs on the left of Fig. 30. The results for a different oil treated with magnesia are shown in the bar graph on the right.

The reduction of fouling and high temperature corrosion is accomplished basically by producing a high melting point ash deposit that is powdery or friable and easily removed by sootblowers or lances. When the ash is dry, corrosion is considerably reduced.

Low temperature sulfuric acid corrosion is reduced by the formation of refractory sulfates by reaction with the SO_3 gas in the flue gas stream. By removing the SO_3 gas, the dew point of the flue gases is sufficiently reduced to protect the metal surfaces. The sulfate compounds formed are relatively dry and easily removed by the normal cleaning equipment.

In general, the amount of additive used should be about equal to the ash content of the fuel oil. In some instances, slightly different proportions may be required for best results, especially for a high temperature corrosion reduction, in which it is generally accepted that the additive should be used in weight ratios of 2:1 or 3:1 (additive/ash), based on the vanadium content of the oil.

Several methods have been successfully used to introduce the additive materials into the furnace. The one in general use consists of metering a controlled amount of an additive oil slurry in the burner supply line. The additive material should be pulverized to 100% through a 325 mesh (44 micron) screen for good dispersion and minimum atomizer wear.

For a boiler fired by a high pressure return flow oil system (Chapter 11), it has been found advantageous to introduce the additive powders by blowing them into the furnace at the desired locations. The powder has to be reduced in size to 100% through a 325 mesh (44 micron) screen for good dispersion.

The choice of a particular additive depends on its availability and cost to the individual plant and the method of application chosen. For example, alumina causes greater sprayer plate wear than the other materials when used in an oil slurry.

The quantity of deposit formed is, of course, an important consideration for each unit from the aspect of cleaning. A comparison of the amounts of deposit

Table 9
Classification of Methods for Controlling Fouling and Corrosion in Oil-Fired Boilers

	Fuel Oil Supply
Reduce amount of fuel ash constituents to the furnace	Selection Blending Purification
	Design
Minimize amounts of fuel ash constituents reaching heat transfer surfaces	Furnace geometry Tube bank arrangement Metal temperature Gas temperature Sootblower arrangement
	Operation
Minimize effects of bonding and corrosive compounds in ash deposits	Load cycle Sootblowing schedule Combustion — excess air Additives Water washing

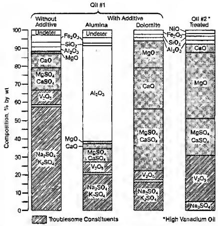


Fig. 30 Effect of fuel oil additives on composition of oil ash deposit.

formed with different additives shows that dolomite produces the greatest quantity because of its sulfating ability, magnesia is intermediate, and alumina and kaolin form the least. However, when adequate cleaning facilities are available, the deposits are easily removed and the quantities formed should not be a problem.

Excess air control

As mentioned previously the problems encountered in the combustion of residual fuel oils – high temperature deposits (fouling), high temperature corrosion and low temperature sulfuric acid corrosion – all arise from the presence of vanadium and sulfur in their highest states of oxidation. By reducing the excess air from 7% to 1 or 2%, it is possible to avoid the formation of fully oxidized vanadium and sulfur compounds and, thereby, reduce boiler fouling and corrosion problems.

In a series of tests on an experimental boiler, it was found that the maximum corrosion rate of type 304 stainless steel superheater alloy held at 1250F (677C) in 2100F (1149C) flue gas was reduced more than 75% (Fig. 31) when the excess air was reduced from an average of 7% to a level of 1 to 2%. Moreover, the ash deposits that formed on the superheater bank were soft and powdery, in contrast to hard, dense deposits that adhered tenaciously to the tubes when the excess air was around 7%. Also, the rate of ash buildup was only half as great. Operation at the 1 to 2% excess air level practically eliminated low temperature corrosion of carbon steel at all metal temperatures above the dew point of the flue gases (Fig. 32). However, much of the beneficial effects of low excess air combustion are lost if the excess air at the burner fluctuates even for short periods of time to a level of about 5%. Carbon loss values for low excess air were approximately 0.5%, which is generally acceptable for electric utility and industrial practice.

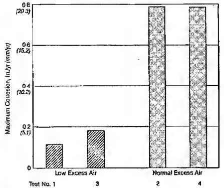


Fig. 31 Effect of low excess air combustion on high temperature oil ash corrosion.

A number of large industrial boilers both in the U.S. and in Europe have been operating with low excess air for several years. As a result, the benefits of reducing low temperature corrosion are well established. However, the benefits on high temperature slagging and corrosion are not wholly conclusive. In any event, great care must be exercised to distribute the air and fuel oil equally to the burners, and combustion conditions must be continuously monitored to assure that combustion of the fuel is complete before the combustion gases enter the convection tube banks.

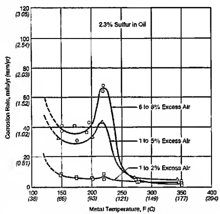
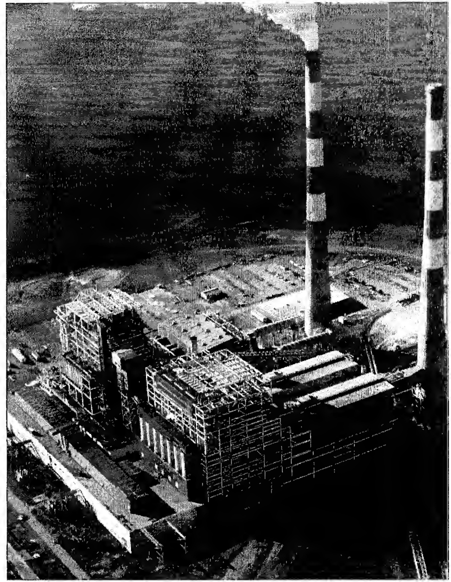


Fig. 32 Effect of excess air on low temperature corrosion of carbon steel.



Two coal-fired boilers: one 685 MW pulverized coal unit and one 844 MW unit with Cyclone™ furnaces